2-9035-1

FTIR-PAS SPECTROSCOPY AS AN ANALYTICAL TOOL FOR STUDY OF BITUMINOUS COALS PHASE II

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DSS CONTRACT REPORT NO. OST83-00347

108 pp

AUG 15 1986

MICROMEDIA

FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY (FTIR-PAS) AS AN ANALYTICAL TOOL FOR EVALUATION OF THE EFFECTS OF WEATHERING AND/OR OXIDATION ON THE COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FINAL REPORT

By

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Work on this project was conducted under the auspices of the Canada Centre for Mineral & Energy Technology.

DSS File Number: 20ST.23440-2-9035/1
DSS Contract Serial Number: OST83-00347
CANMET Project Number:
CANMET SCIENTIFIC AUTHORITY: Dr. J. A. MacPhee

DATE: April 1985

This report should be cited as DSS Contract Report No. OST83-00347.

AUG 15 1986
MICROMEDIA

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

SUMMARY

This report incorporates and supplements the interim progress reports submitted to the Scientific Authority over the time period of the Contract.

The aspects studied are defined broadly as the examination of various samples of fossil fuels and their products of chemical modification by PhotoAcoustic Fourier Transform InfraRed (PAIFT) spectroscopy, and the analytical uses to which the results of such examinations may be put.

Specific types of samples examined included the following classes:

1. Partially burnt vitrinites from combustions at 1200°C
2. Products of chemical modification (derivatization, demineralization) of sub-bituminous coals by carbon monoxide and water at various temperatures.
3. Asphaltenes from various oil-sands bitumens subjected to various thermal and demineralization treatments
4. Bituminous coals oxidized at low (50°C) temperatures under elevated air pressure (approximately 1400 kPa)
5. Surface-oxidized samples of bituminous coals obtained by simple laboratory storage
6. Vacuum thermolysis of surface-oxidized coals
7. Products from treatment of surface-oxidized coals with phase-transfer basic reagents
8. Oxidation products from the reagent system air/tetrahydrofuran + aqueous tetrabutylammonium hydroxide.

INTRODUCTION

Examination by PAIFT spectroscopy overcomes the major inherent disadvantages of DRIFT and KBr-pellet transmission spectroscopies in that the necessity is eliminated for sample preparation by fine subdivision. Thus it is possible to monitor changes occurring at the actual surface of the material being studied.

In earlier reports (1-3), we have shown that the changes occurring on oxidation of coals may be revealed by automated spectral subtraction routines. In one aspect of the present study, we have sought to increase the sensitivity of detection of introduced functional groups in coals which have been oxidized for brief periods at relatively low temperatures.

Subtractive procedures may also be used to isolate the changes accompanying chemical derivatization (such as quantitative methylations and/or acetylations) and to reveal the nature and proportion of mineral-matter content in samples.

PAIFT SPECTRA OF PARTIALLY BURNT VITRINITE SAMPLES

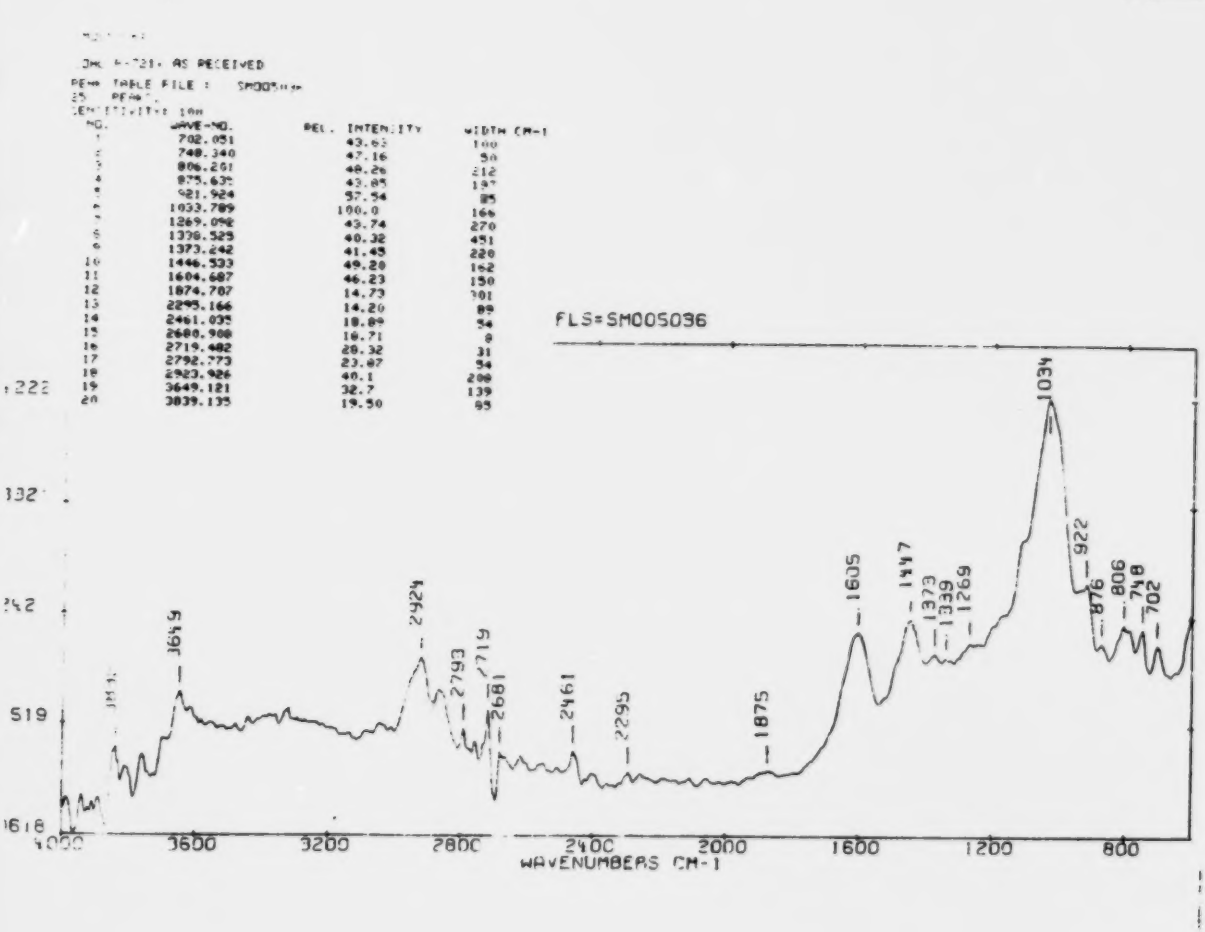
A series of "unburnt" pyrolysed samples derived from rapid passage of the bituminous coals P-721 through P-724 through a 1200^{o} reactor was examined. The spectral information, consisting of spectral display and digital peak printouts for the (demineralized) pyrolysed materials is reproduced in the following Figures.

A copy of the commentary on these spectra is provided as Table 1.

Additional commentary can now be made: the sample P-721 is much richer in mineral matter than the other samples, so that it is essential to undertake demineralization of this sample; the mineral content of the other samples is not high enough to influence the resulating spectra.

The high level of the black-body (unresolved) signal reflects the largely coke-like nature of the pyrolysed material.

FIGURE 1
COAL P-721, AS-RECEIVED



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FIGURE 2
COAL P-722, AS-RECEIVED

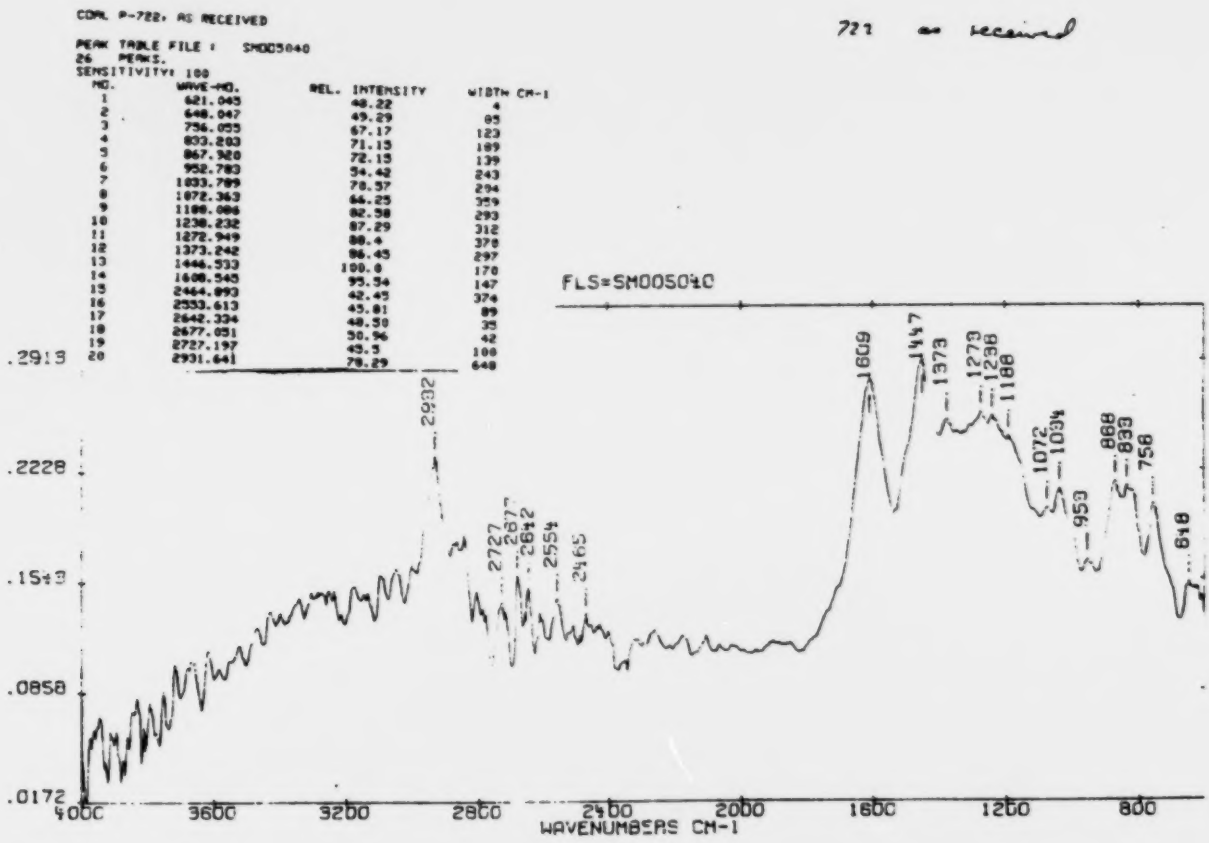


FIGURE 3
COAL P-723, AS-RECEIVED

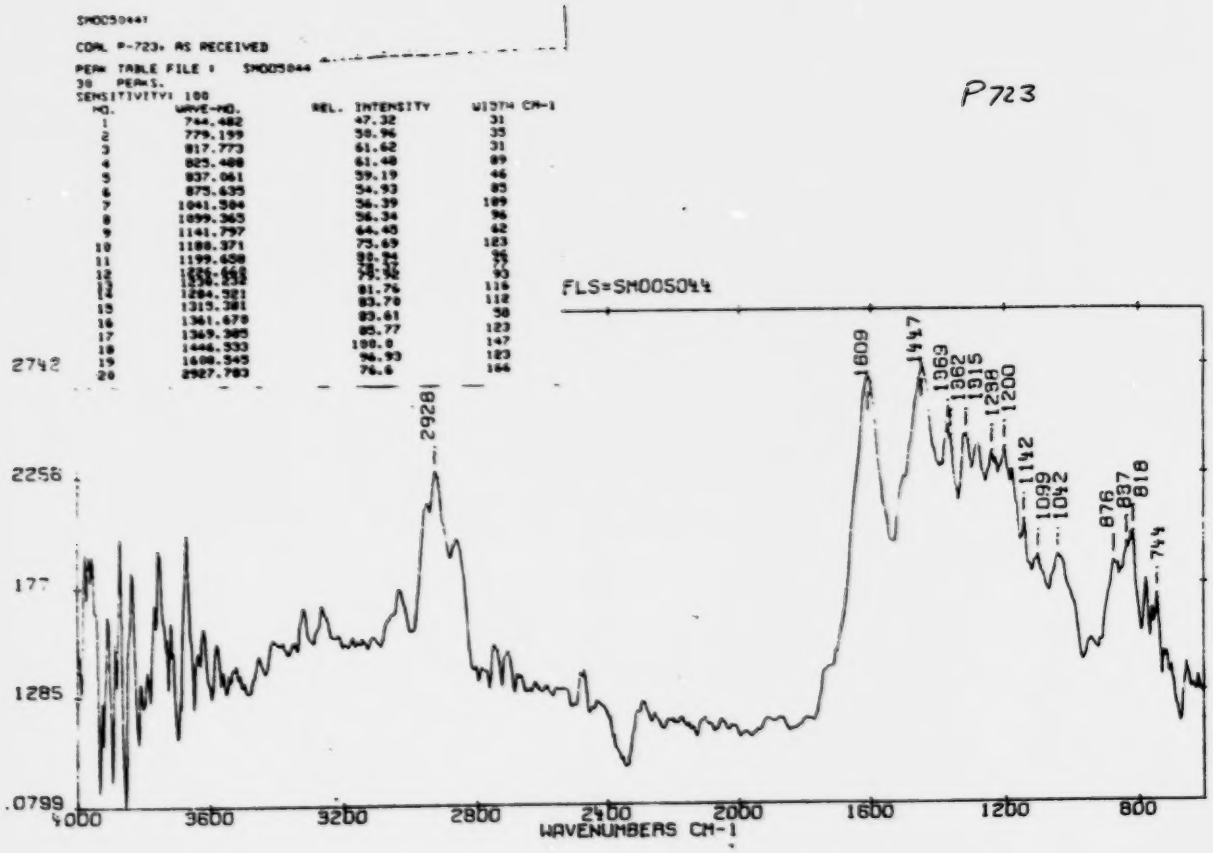


FIGURE 4

COAL P-724, AS-RECEIVED

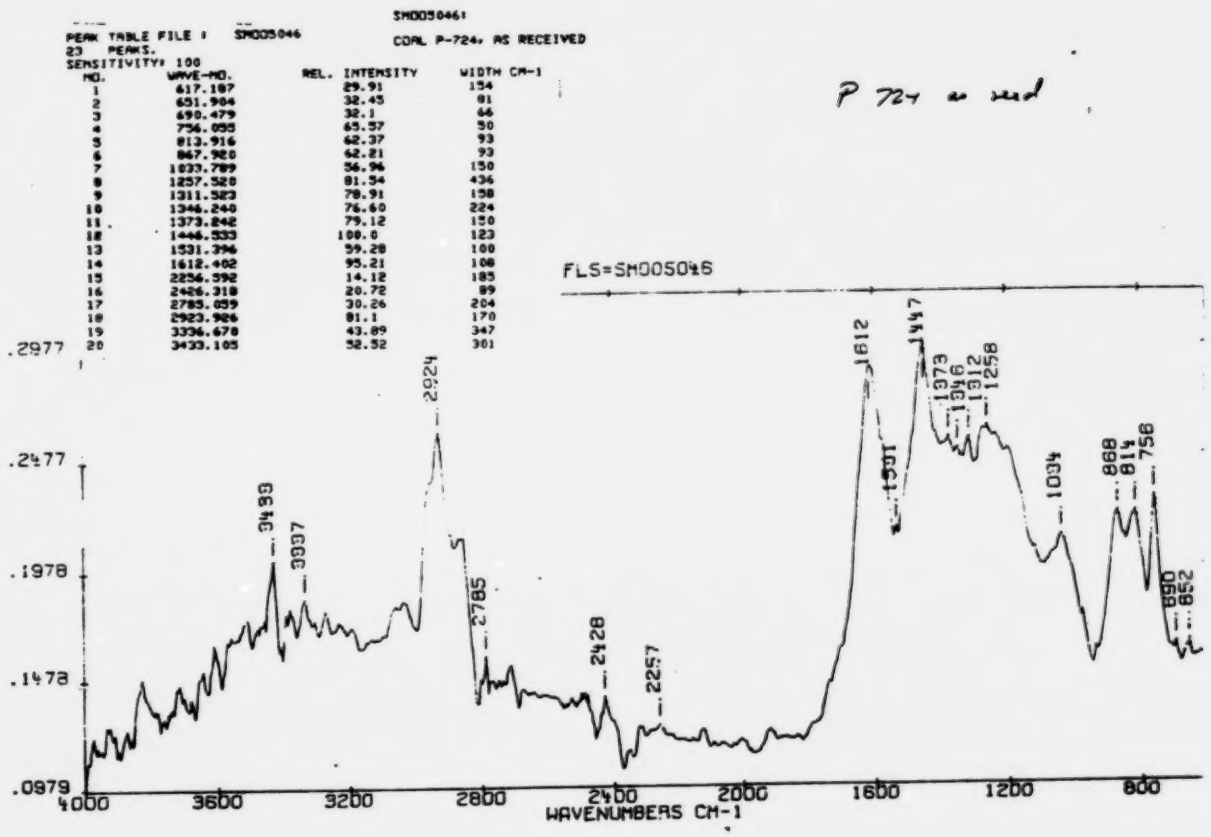


FIGURE 5

DEMINERALIZED COAL P-721

DEMINERALIZED COAL P-721

PEAK TABLE FILE : SM005050
30 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	665.615	44.24	69
2	681.045	45.20	104
3	648.047	47.93	85
4	705.908	49.17	46
5	759.912	61.25	77
6	790.771	60.56	23
7	810.059	69.25	224
8	864.042	64.13	147
9	1029.932	78.23	130
10	1118.652	78.34	154
11	1199.659	85.86	339
12	1234.373	89.60	135
13	1253.662	84.26	177
14	1272.949	93.17	123
15	1307.666	98.80	66
16	1319.238	97.79	270
17	1373.242	84.82	239
18	1446.533	100.0	134
19	1608.345	99.60	131
20	2923.926	80.39	177

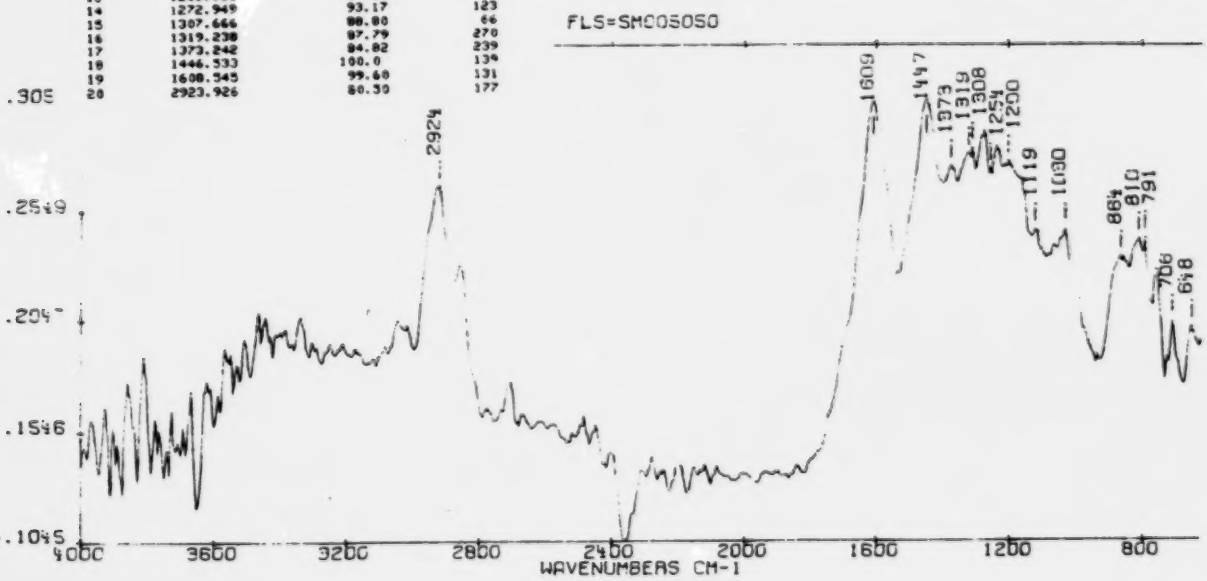
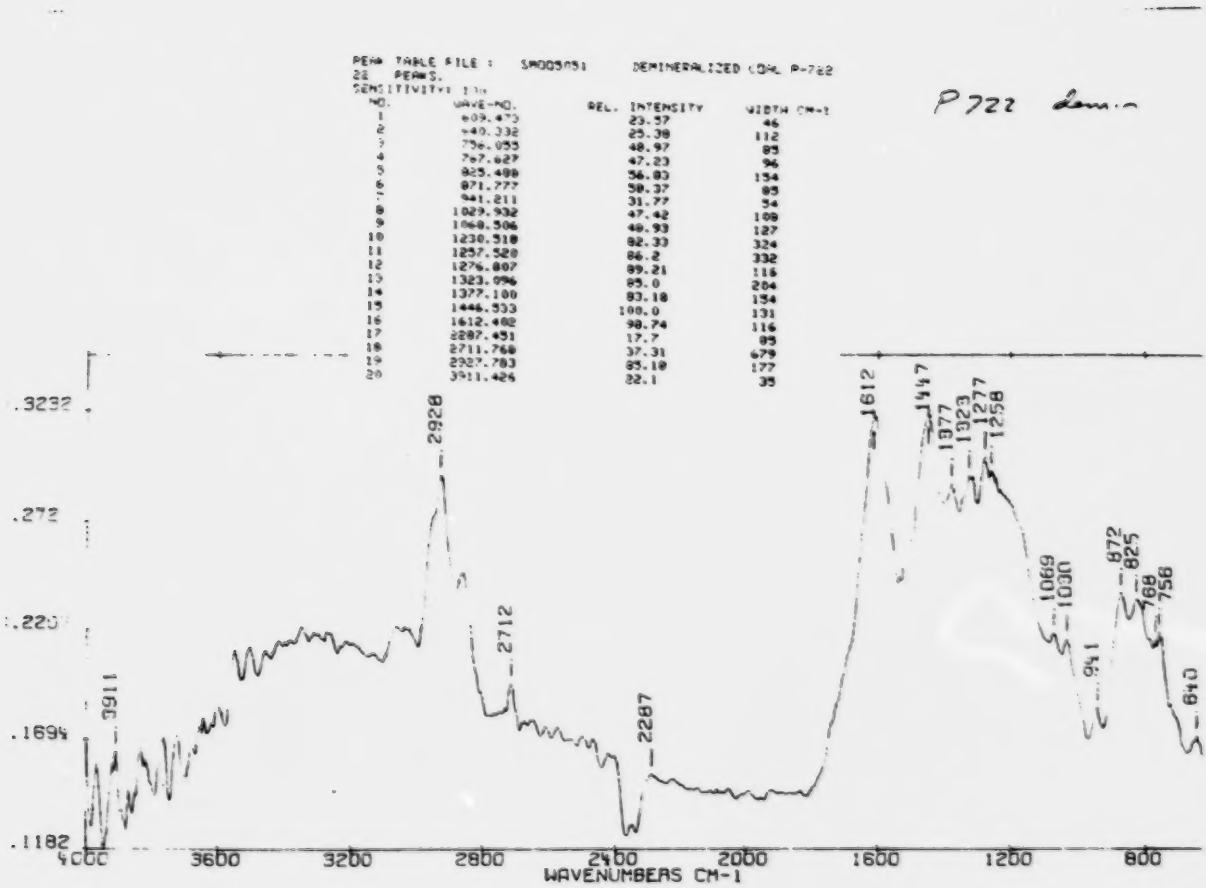
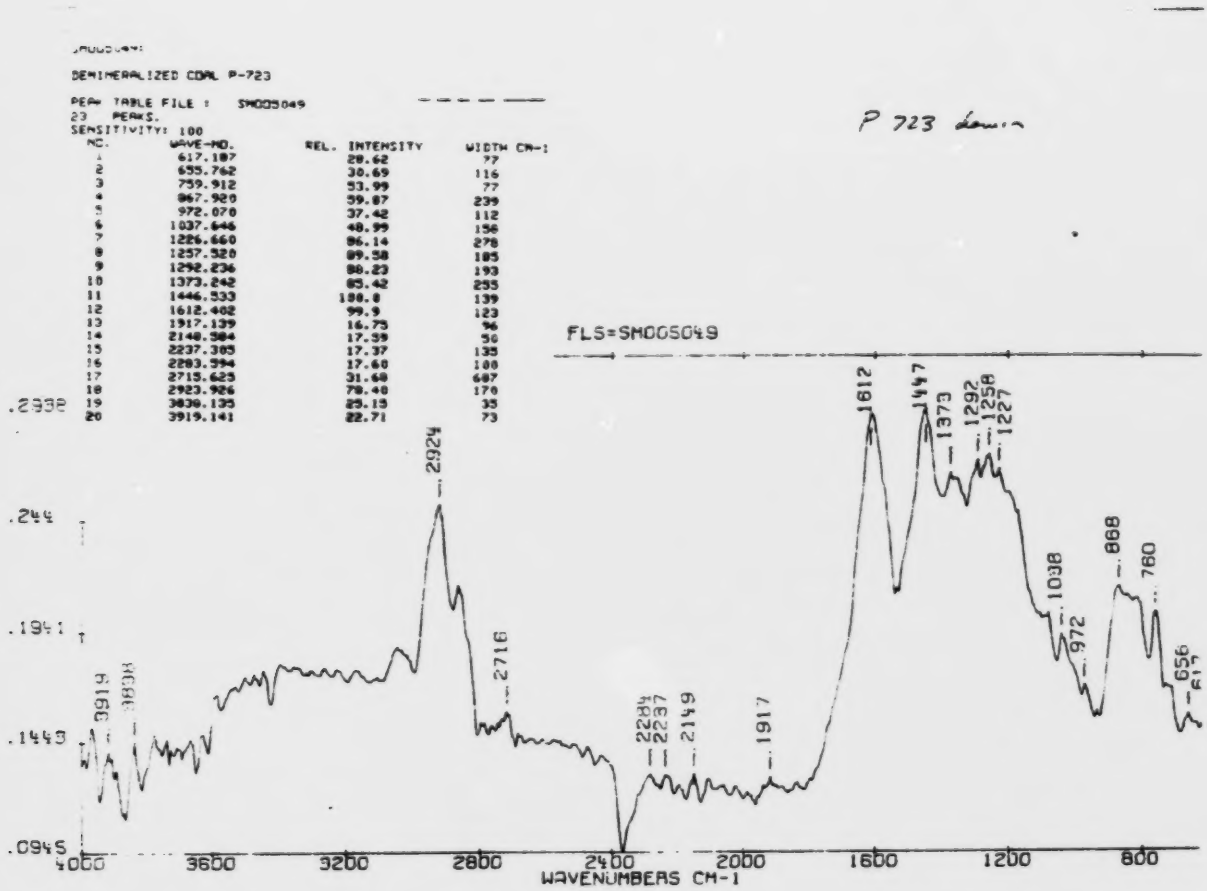


FIGURE 6
DEMINERALIZED COAL P-722



10

FIGURE 7
DEMINERALIZED COAL P-723



11

FIGURE 8
DEMINERALIZED COAL P-724

DEMINERALIZED COAL P-724

PEAK TABLE FILE : SM005048
27 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	617.187	31.52	46
2	629.760	30.40	69
3	651.904	30.40	100
4	767.627	38.41	127
5	829.346	64.92	127
6	867.920	63.10	93
7	941.211	33.99	46
8	1211.230	82.12	274
9	1276.807	90.75	174
10	1299.951	93.22	89
11	1334.668	86.25	85
12	1369.385	82.18	297
13	1446.333	100.0	162
14	1612.482	99.8	108
15	2711.768	47.97	35
16	2927.783	78.44	170
17	3386.816	45.73	478
18	3668.408	35.58	69
19	3757.129	28.36	128
20	3841.992	32.67	93

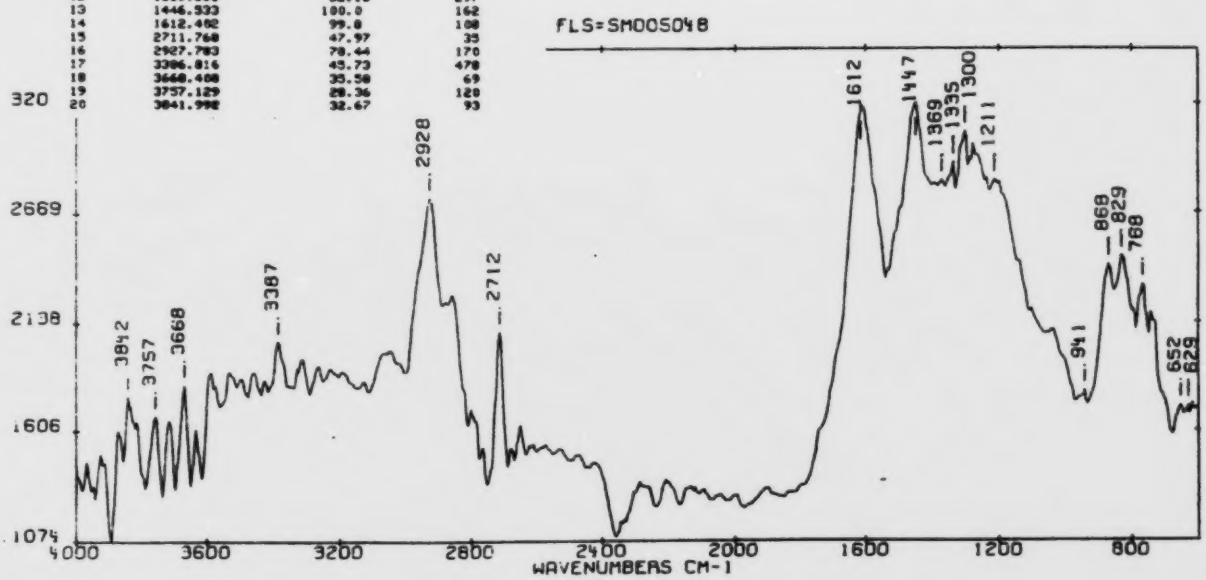


FIGURE 9
UNBURNT P-721

MASS8427 = UNBURNT P-721, PASS @ 1200 DEG.

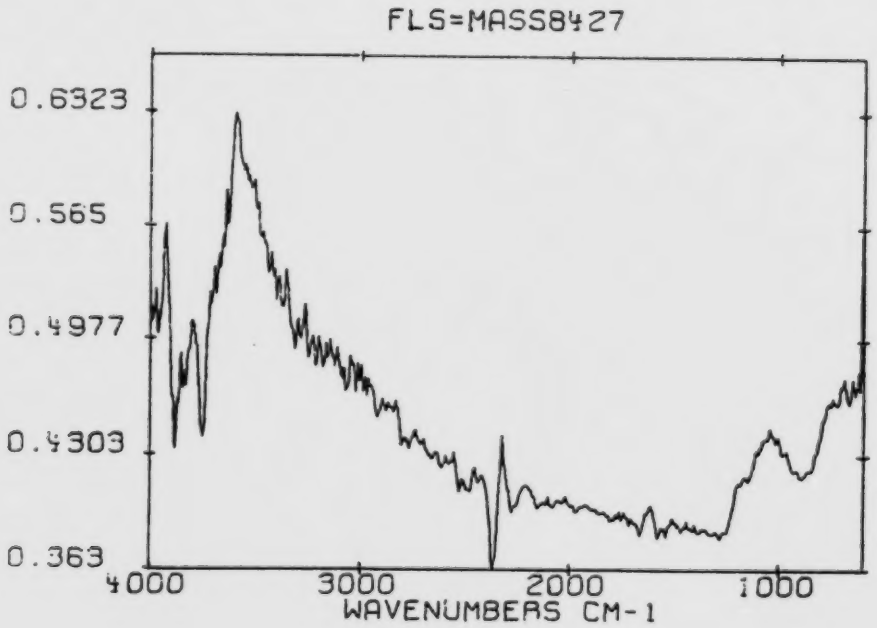


FIGURE 10
UNBURNT P-722

MASS8430 = UNBURNT P-722, PASS @ 1200 DEG.

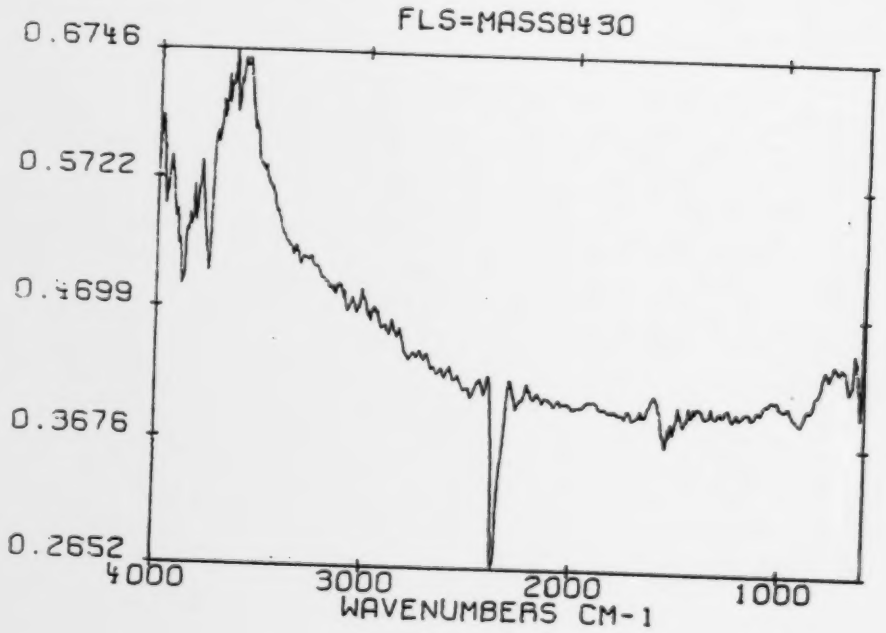


FIGURE 11
UNBURNT P-723

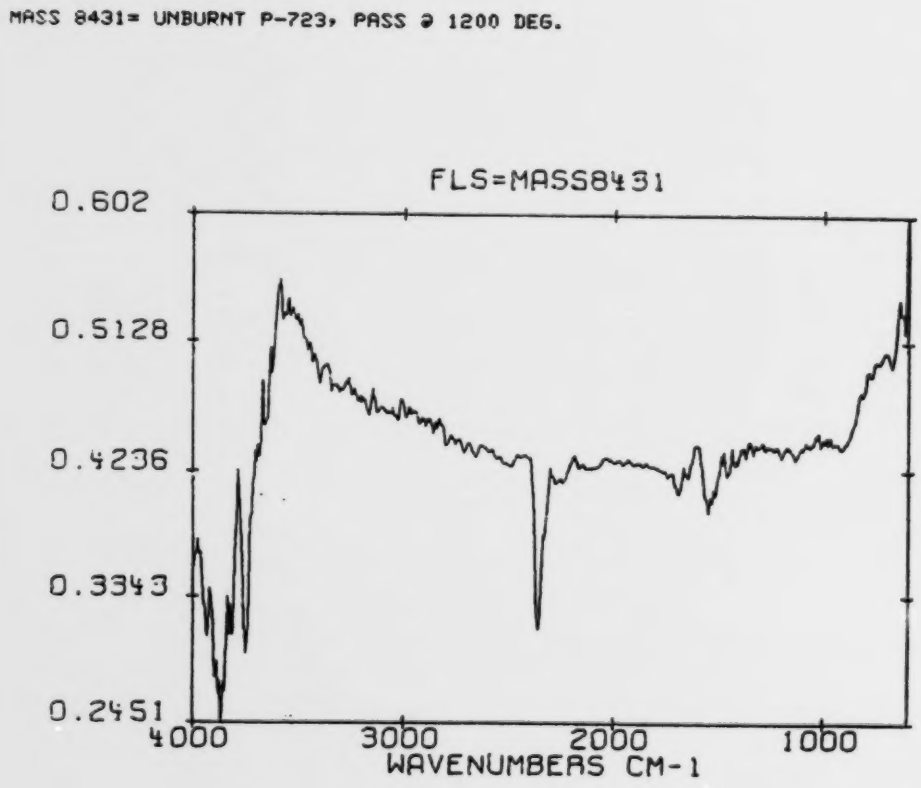


FIGURE 12
UNBURNT P-724

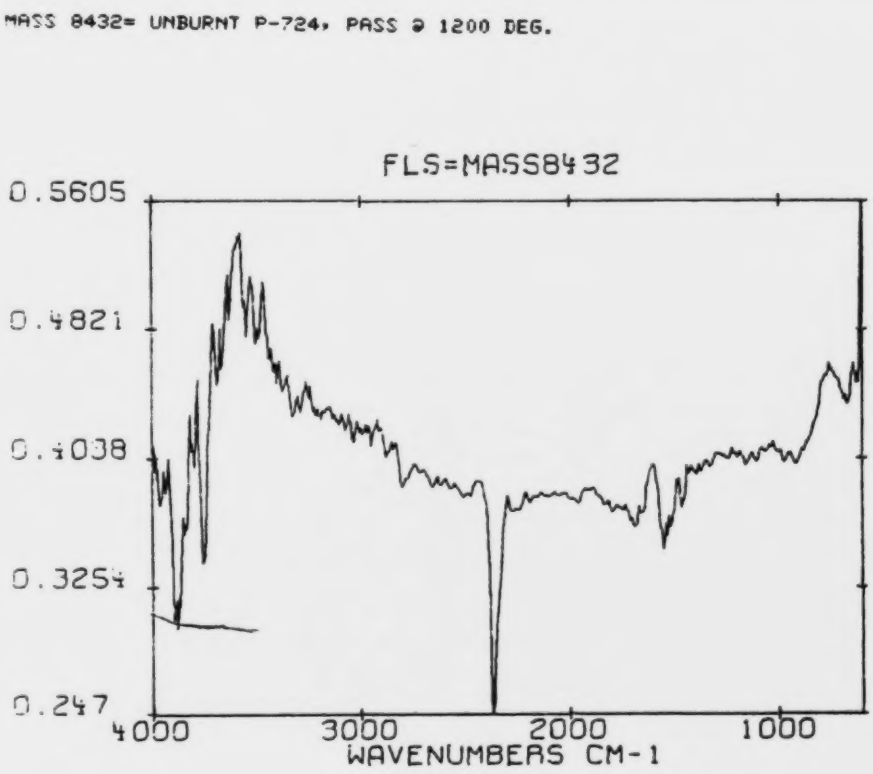


FIGURE 13
DEMINERALIZED UNBURNT P-721

SM005144:
DEMINERALIZED UNBURNT P-721, PASS @ 1200 DEG.

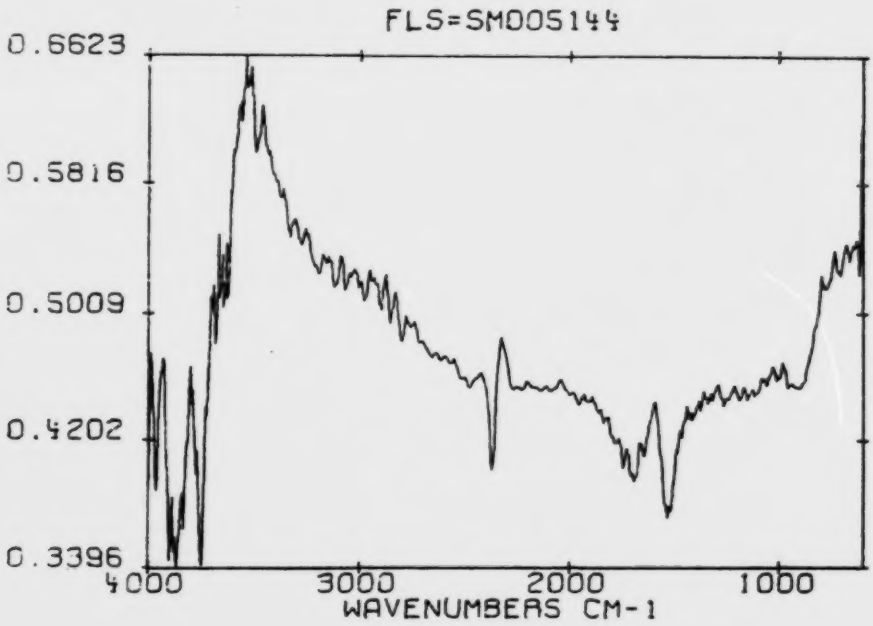


FIGURE 14
DEMINERALIZED UNBURNT P-722

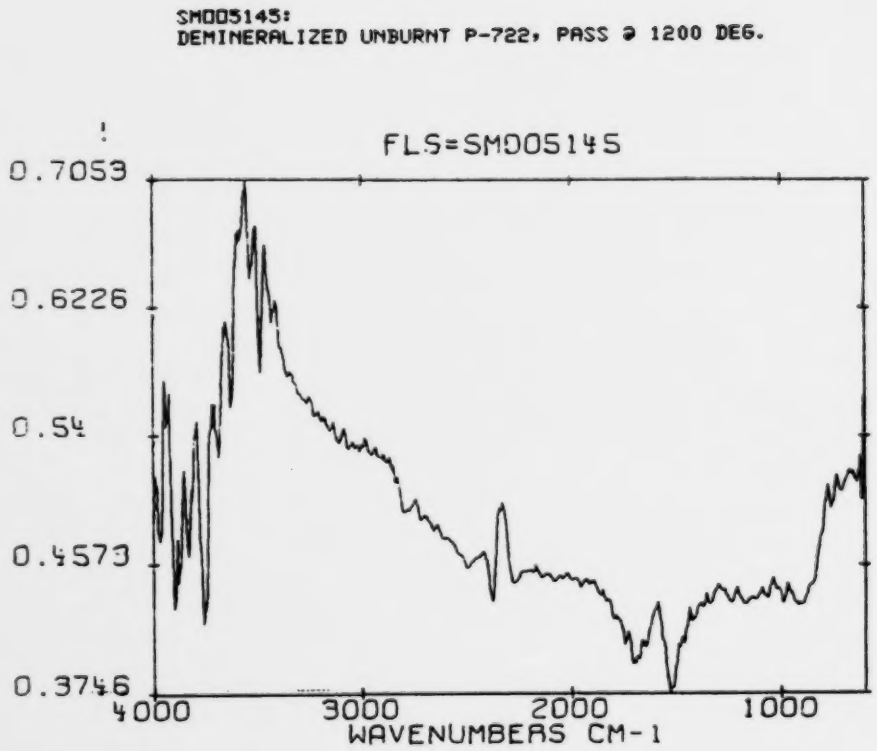


FIGURE 15
DEMINERALIZED UNBURNT P-723

SM005146:
DEMINERALIZED UNBURNT P-723, PASS @ 1200 DEG.

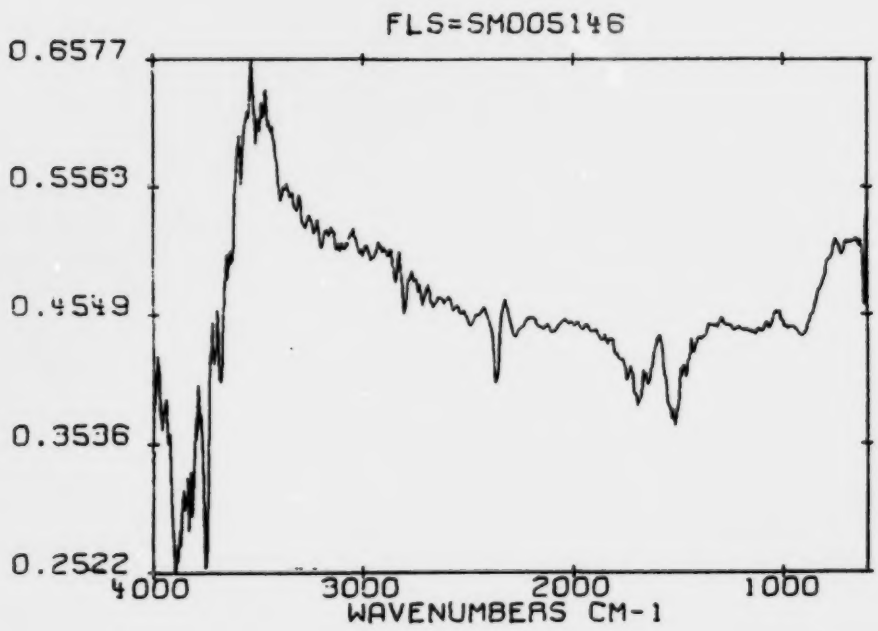


FIGURE 16
DEMINERALIZED UNBURNT P-724

SM005147:
DEMINERALIZED UNBURNT P-724, PASS @ 1200 DEG.

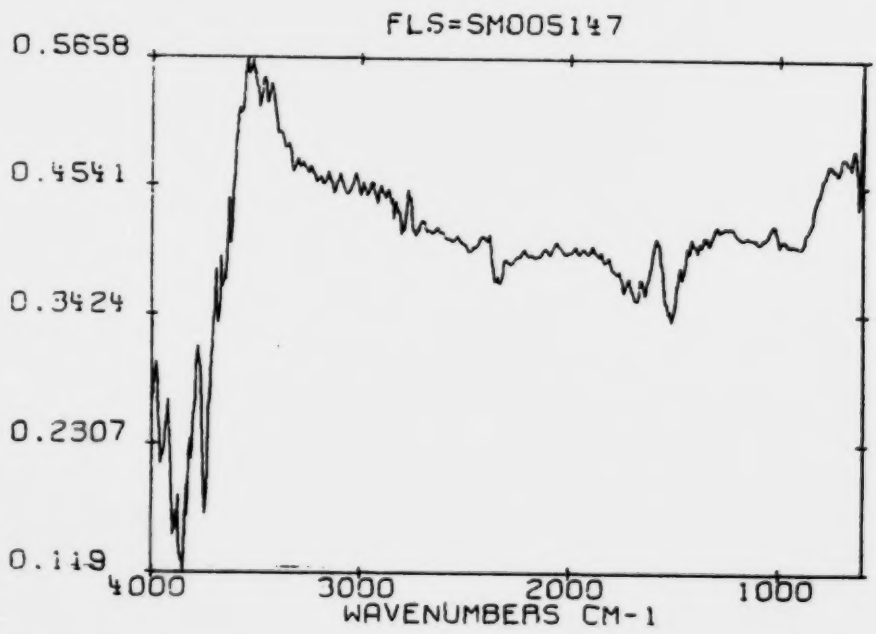


FIGURE 17
BASELINE-CORRECTED PARTIAL SPECTRUM (1750-1400 CM^{-1}),
DEMINERALIZED UNBURNT P-721

BALI 5144:
BASELINE-CORRECTED, FROM 1750-1400 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-721 (#8427) FROM PASS @ 1200 DEG

PEAK TABLE FILE : BALI5144
16 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	1593.115	100.0	58
2	1616.260	89.77	39
3	1724.268	88.20	81
4	1666.406	81.86	23
5	1627.832	80.73	62
6	1654.834	79.84	31
7	1438.818	69.50	42
8	1697.266	64.29	39
9	1677.979	61.54	112
10	1454.248	61.7	23
11	1685.693	59.66	69
12	1415.674	59.40	62
13	1469.678	56.84	35
14	1488.965	45.98	31
15	1539.111	13.25	8

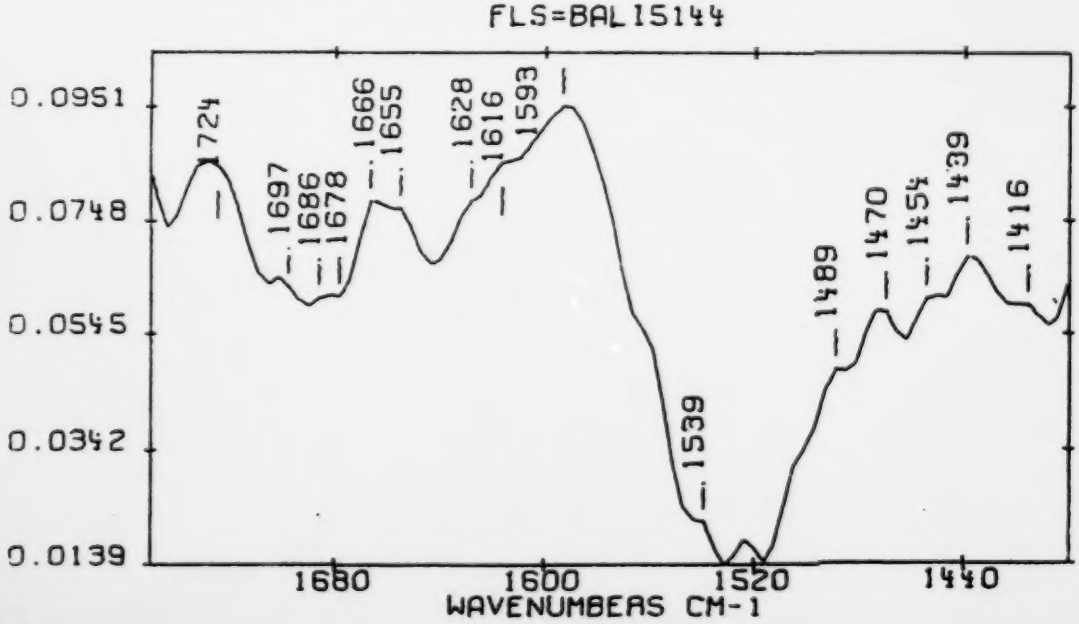


FIGURE 18
BASELINE-CORRECTED PARTIAL SPECTRUM (1750-1400 CM^{-1}),
DEMINERALIZED UNBURNT P-722

BAL15145:
BASELINE-CORRECTED, FROM 1750-1400 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-722 (#8430) FROM PASS @ 1200 DEG

PEAK TABLE FILE : BAL15145
17 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	1731.982	100.0	66
2	1589.258	99.82	42
3	1600.830	96.29	131
4	1616.260	91.48	39
5	1627.832	83.50	31
6	1666.406	79.50	23
7	1654.834	75.60	62
8	1685.693	67.42	69
9	1697.266	66.42	66
10	1438.818	64.77	31
11	1562.256	57.79	31
12	1415.674	50.61	62
13	1454.248	48.57	23
14	1469.678	43.56	39
15	1488.965	40.47	31

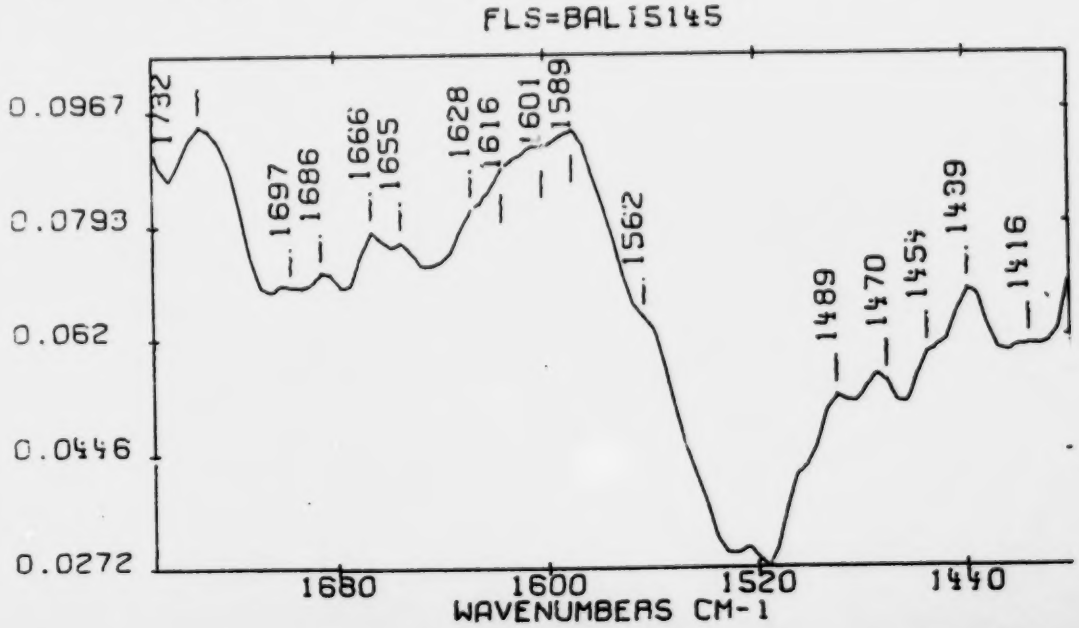


FIGURE 19
BASELINE-CORRECTED PARTIAL SPECTRUM (1750-1400 CM^{-1}),
DEMINERALIZED UNBURNT P-723

BAL15146:
BASELINE-CORRECTED, FROM 1750-1400 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-723 (#8431) FROM PASS @ 1200 DEG

P1 PPO AFA=BAL15146#

PEAK TABLE FILE : BAL15146
16 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	1593.115	100.0	66
2	1724.268	90.25	35
3	1735.840	89.70	39
4	1616.260	86.91	31
5	1666.406	77.80	15
6	1627.832	75.23	46
7	1438.818	73.12	23
8	1654.834	72.7	27
9	1404.102	68.44	54
10	1415.674	65.12	31
11	1704.980	60.48	46
12	1677.979	55.49	62
13	1454.248	54.99	15
14	1477.393	53.39	39
15	1488.965	51.18	15

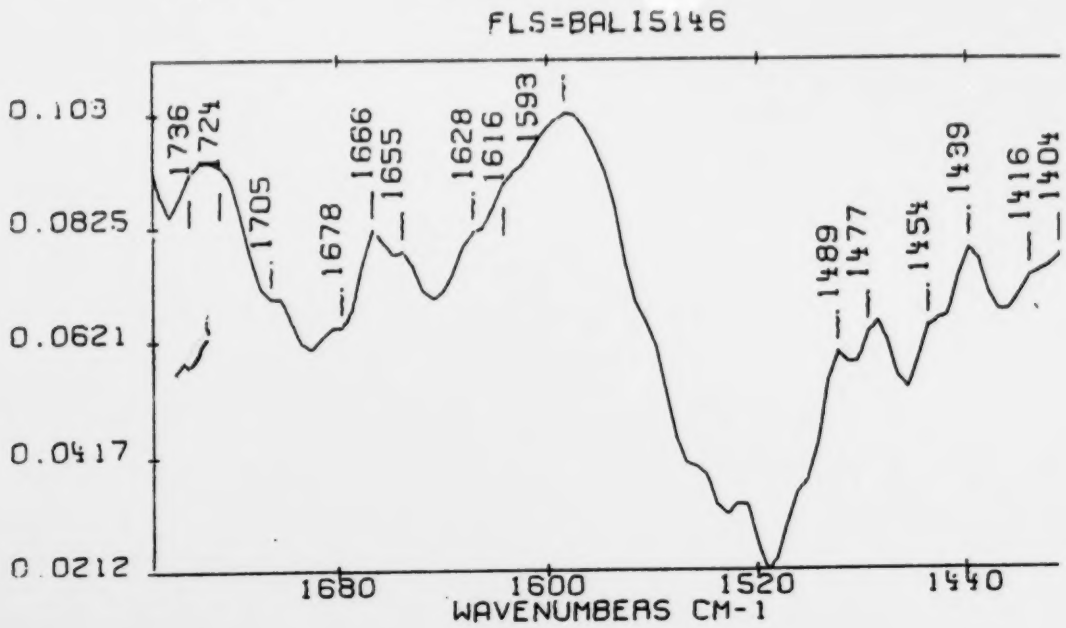


FIGURE 20
BASELINE-CORRECTED PARTIAL SPECTRUM (1750-1400 CM^{-1}),
DEMINERALIZED UNBURNT P-724

BALI5147:
BASELINE-CORRECTED, FROM 1750-1400 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-724 (#8432) FROM PASS @ 1200 DEG

P1 PPO AFA=BALI5147#

PEAK TABLE FILE : BALI5147
16 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	1585.400	100.0	66
2	1415.674	76.41	31
3	1716.553	74.75	23
4	1724.268	73.64	85
5	1616.260	71.59	31
6	1434.961	70.24	39
7	1666.406	66.40	15
8	1654.834	64.1	39
9	1427.246	63.11	289
10	1627.832	61.60	39
11	1697.266	57.72	23
12	1473.535	53.64	27
13	1677.979	47.13	58
14	1488.965	36.77	15
15	1539.111	25.86	12

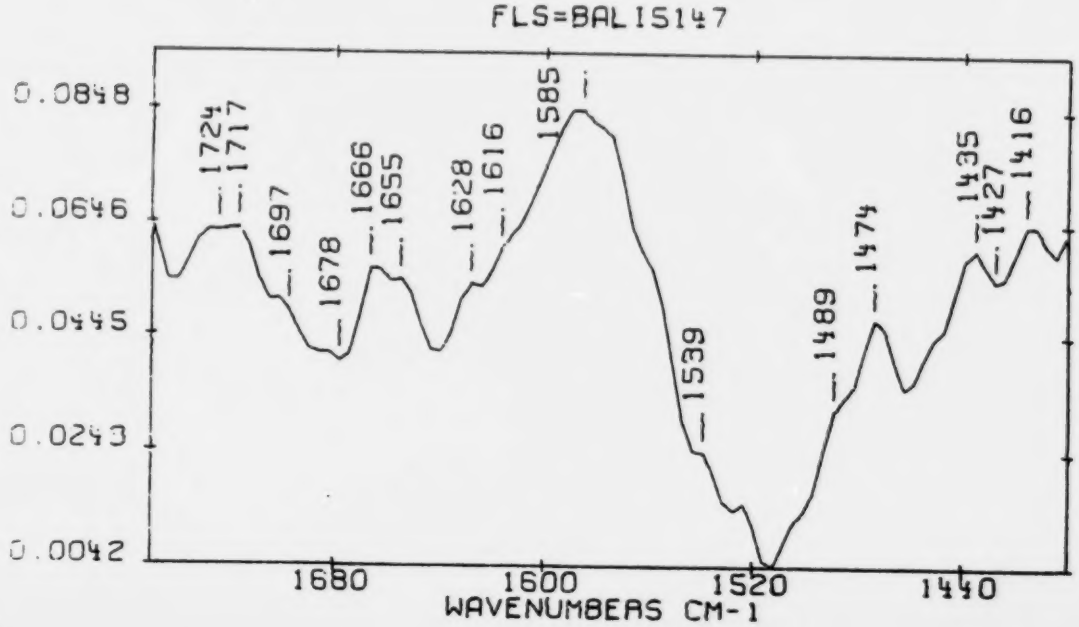


FIGURE 21
BASELINE-CORRECTED PARTIAL SPECTRUM (900-625 CM^{-1}),
DEMINERALIZED UNBURNT P-721

BALA5144:
BASELINE-CORRECTED, FROM 900-625 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-721 (8427) FROM PASS @ 1200 DEG.

PEAK TABLE FILE : BALA5144
10 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	794.629	100.0	31
2	732.910	99.8	46
3	678.906	76.55	54
4	763.770	70.66	81
5	640.332	55.85	54
6	655.762	53.93	31
7	648.047	53.57	100
8	829.346	48.6	23
9	848.633	23.47	39
10	887.207	3.46	8

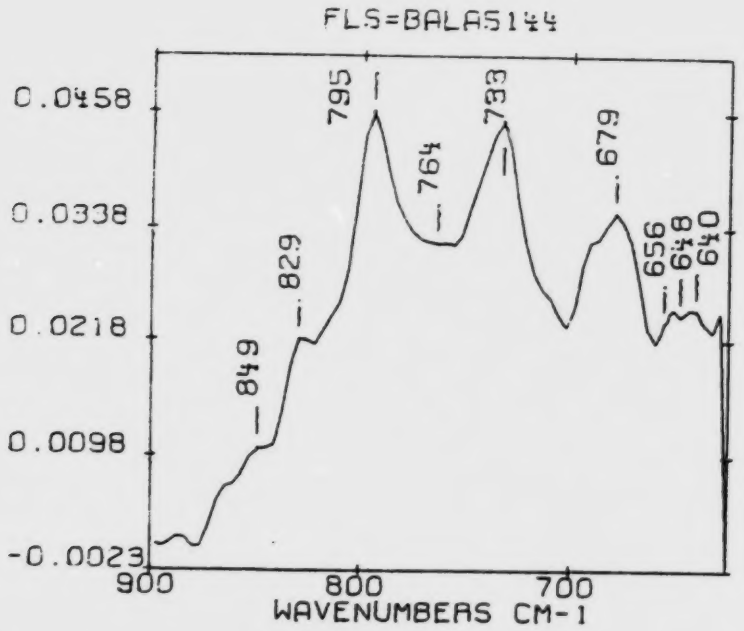


FIGURE 22
BASELINE-CORRECTED PARTIAL SPECTRUM (900-625 CM^{-1}),
DEMINERALIZED UNBURNT P-722

BALA5145:
BASELINE-CORRECTED, FROM900-625 CM.-1
DEMINERALIZED SAMPLES OF UNBURNT P-722 (#8430) FROM PASS @ 1200 DEG.

F1 PPO AFA=BALA5145#

PEAK TABLE FILE : BALA5145
9 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	775.342	100.0	54
2	732.910	93.27	46
3	678.906	71.0	58
4	667.334	67.88	31
5	690.479	67.9	54
6	709.766	63.9	39
7	651.904	60.83	19
8	640.332	45.9	123
9	867.920	10.91	8

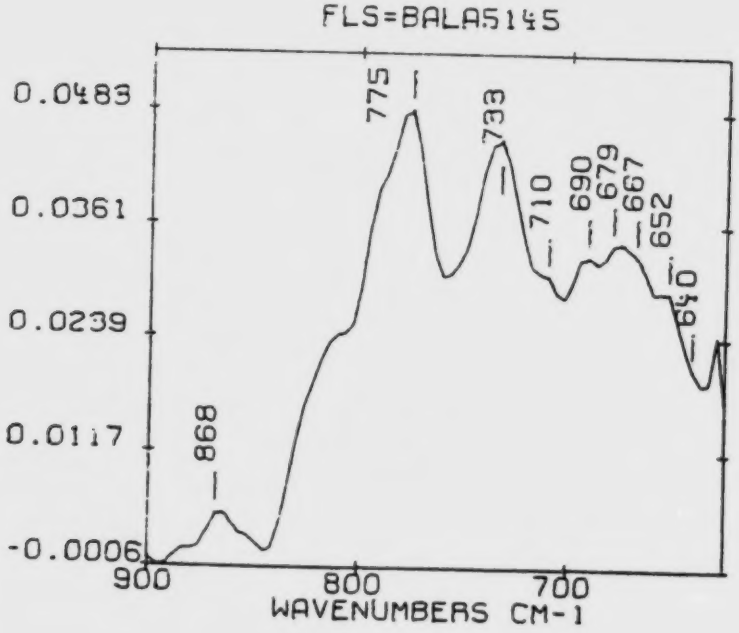


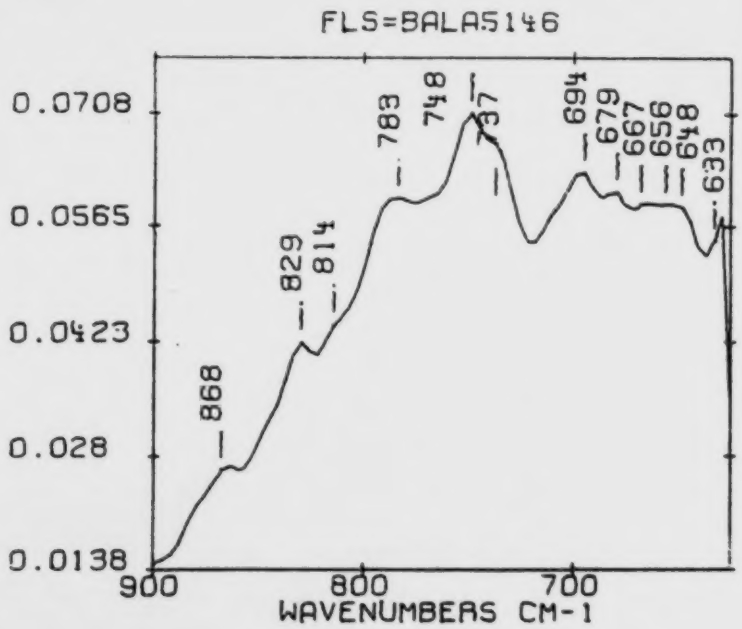
FIGURE 23
BASELINE-CORRECTED PARTIAL SPECTRUM (900-625 CM^{-1}),
DEMINERALIZED UNBURNT P-723

BALA5146:
BASELINE-CORRECTED, FROM 900-625 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-723 (#8431) FROM PASS @ 1200 DEG.

P1 PPD AFA=BALA5146#

PEAK TABLE FILE : BALA5146
13 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	748.340	100.0	46
2	736.768	92.82	42
3	694.336	86.85	77
4	678.906	82.44	77
5	655.762	80.40	108
6	783.057	80.39	69
7	667.334	80.5	104
8	648.047	78.25	62
9	632.617	72.2	46
10	813.916	54.12	31
11	829.346	50.25	39
12	867.920	22.68	23
13	894.922	2.84	8



BALA5147:
BASELINE-CORRECTED, FROM 900-625 CM.-1
DEMINERALIZED SAMPLE OF UNBURNT P-724 (=8432), FROM PASS 2, 1200 DSG

FIGURE 24

BASELINE-CORRECTED PARTIAL SPECTRUM (900-625 CM^{-1}),

DEMINERALIZED UNBURNT P-724

R1 PPO AFA=BALA5147=

PEAK TABLE FILE : BALA5147
14 PEAKS.
SENSITIVITY: 100

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	759.912	100.0	62
2	640.332	99.7	39
3	694.336	97.73	46
4	748.340	95.92	73
5	686.621	95.72	69
6	729.053	88.37	35
7	783.057	84.22	85
8	667.334	83.66	93
9	659.619	81.84	35
10	717.480	76.98	312
11	810.059	63.34	54
12	852.490	22.89	31
13	864.062	20.7	23
14	891.064	2.8	8

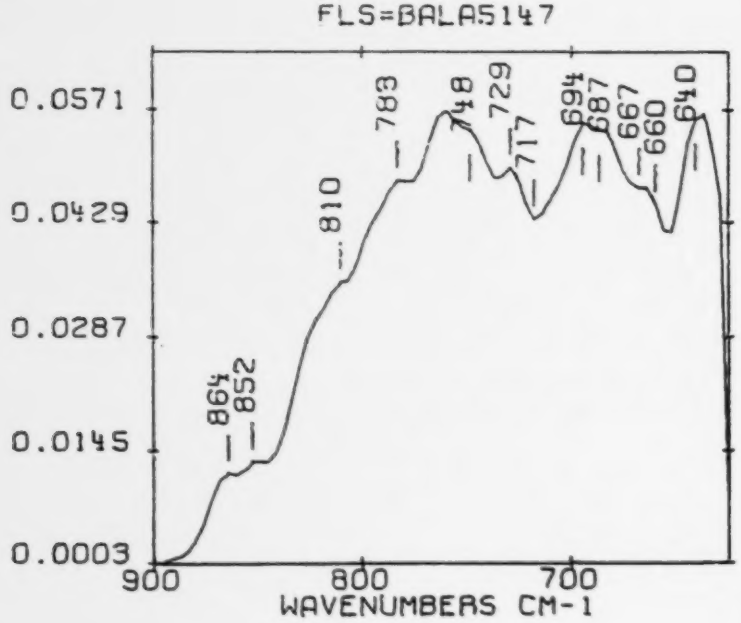


TABLE 1

DEPARTMENT OF CHEMISTRY, ST. FRANCIS XAVIER UNIVERSITY
ANTIGONISH, NOVA SCOTIA B2G 1C0

1984 June 5

Dr. J. A. MacPhee
Energy Research Laboratories, CANMET
Energy, Mines and Resources Canada
555 Booth Street, Ottawa

Dear Tony:

We have examined the series of "unburnt" pyrolysed samples derived from the coals P-721 through P-724, and I enclose the detailed spectra for your consideration. For comparison purposes, the spectra of the original coals are also enclosed, although the comparisons will not be very meaningful.

Firstly, I want to point out that the unburnt samples give spectra indicative of appreciable carbonization, and the unresolved or black-body absorption throughout the spectrum is quite high. Typically, the minimum absorption is 25-35 % of the charcoal reference, whereas for a normal coal it might be 5 %. The uncorrected spectra are displayed as MASS8427-8432 and those for the demineralized samples as SM005144-5147. The main features are in the O-H stretch region around 3600 cm.-1, a discrete peak centred around 1600 cm.-1 with minima to either side, and in the aromatic C-H deformation region.

However, without some ennancement procedure, the spectra are not very informative. In order to maximize the displayed information content within the recorded spectra, we used a baseline-correction subroutine in the 1400-1750 and 625-900 cm.-1 regions (the baseline-correction process divides the region examined into 32 sectors, and in effect, "pulls a string" along the curves fitted by minima or found peaks: the end results amount to peak enhancement relative to the unresolved background). The enhanced subspectra (for the demineralized samples only) are enclosed as the series prefixed "BALI" and "BALA", together with appropriate peak printouts.

In the "BALI" series, the features from 1710-1740 and 1655-1665 cm.-1 (likely carboxylic acid and diaryl ketone or quinone) are nicely resolved, and in the "BALA" series, the spectra of the samples derived from coals P-721 and P-722 are closely similar to one another, as are those from P-723 and P-724 (but different from the first two).

I feel that this manipulative procedure has worked pretty well, and if we are smart enough, could be correlated with some physical properties of the samples. However, any quantitative chemical derivatization of these samples would be difficult (we have failed to acetylate them using conventional procedures). Anyway, let me have your thoughts on this point.

We feel that a useful series to be examined next would be from the interrupted thermogravimetry of samples related to those just examined, if such are available.

We had hoped to be able to visit Ottawa during the summer, but my wife is having some quite serious problems with a heart arrhythmia, and for the next month or so I will wish to stay pretty close to home.

With best wishes,

Yours sincerely,

Brian

Brian M. Lynch

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MODIFICATION OF LIGNITES BY TREATMENT WITH CO/H_2O

The sample examined was sub-bituminous coal P-668, which possessed the following analytical characteristics:

proximate analysis (dry) (wt. %)
Ash 7.65
Volatile matter 35.92
Fixed carbon 56.43

ultimate analysis
C 67.93 %
H 4.65
S 0.11
N 0.82
Ash 7.65
O (by difference) 18.84

Ash analysis
SiO_2 1.98 %
Al_2O_3 1.51
Fe_2O_3 0.38
CaO 1.79
Heating value 25.92 MJ/Kg

Samples 84-138 through 84-142 were obtained by treatment of P-668 (10 g) with water (2 g) under CO pressure (1500 psi at 25°C) for varying times at specified temperatures.
The text of an interim report, submitted 1985 January 24, is incorporated as Tables 2-4. Spectra of the various samples are reproduced commencing with Figure 25.

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

TABLE 2

Interim report, 1985 January 24

ST. FRANCIS XAVIER UNIVERSITY
ANTIGONISH, NOVA SCOTIA
B2G 1C0
DEPARTMENT OF CHEMISTRY

1985 January 24

Dr. J. A. MacPhee
Research Scientist
CANMET/Energy Research Laboratories
Energy, Mines, and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1

Dear Tony:

I enclose the PA-FTIR spectra of the variously treated samples of the P-668 lignite, together with the species which we have derivatized by acetylation. In addition, we have demineralised the majority of the samples by treatment with HCl-HF and have then acetylated them.

Your information identified the samples as follows, and the spectra numbers are tabulated to accompany these:

Sample Identification

1. untreated coal P-668

10-G Samples with 2 g water were pressurized with CO to 1500 psi at 25C and heated for the indicated times:

2. 84-138 1 h at 400C
3. 84-139 2 h at 375C
4. 84-140 2 h at 360C
5. 84-141 0.3h at 360C
6. 84-142 2 h at 345C

Spectra numbers:

Sample/as received/acetylated/demineralised/then acetylated			
1. P-668 /5704	/5718	5744	5747
2. 84-138/5711	/5729	5743	5748
3. 84-139/5706	/5751		
4. 84-140/5707	/5730		
5. 84-141/5708	/5720	5742	5750
6. 84-142/5709	/5731	5741	5749

Although the spectra of the coals themselves look fairly similar, there are systematic differences. Samples 84-138 and 84-139 are similar to one another, as are 84-140 and 84-142. The differences lie in the presence of added mineral-matter peaks at approximately 1435 and 1470 cm^{-1} in the coals treated at the higher temperatures (84-138 and 84-139). I assign these peaks as arising from a basic carbonate.

This is best revealed by subtractive spectra of the as-received versus the demineralised samples (Figure "MINERAL CONTENT") enclosed).

Thus for the original P-668 the significant variations with demineralisation are a negative-going peak corresponding to an increased carboxylic acid content in the demineralised coal, and a positive feature around 1050 cm^{-1} reflecting the clay minerals in the as-received coal. For 84-138, the negative-going peak is absent (since the coal has undergone decarboxylation), the feature around 1050 cm^{-1} is still evident, and the basic carbonate doublet around 1450 cm^{-1} appears.

TABLE 3

Interim report, 1985 January 24, continued

Considerable decarboxylation occurs for all the treated coals; this may be estimated from difference spectra on the various demineralized samples covering the carboxylic acid stretch region (demineralization converts carboxylate species into carboxylic acids). Thus the figures DMCA5741, 5742, 5743 are obtained by subtracting the spectra of demineralized 84-142, 84-141, and 84-138 from that of demineralized coal P-668.
The differences in the photoacoustic energy ordinate (the "y" axis) from the software-defined baseline are:

0.0628 84-142 (DMCA5741)
0.0468 84-141 (DMCA5742)
0.0797 84-138 (DMCA5743).

The magnitudes of these are certainly in the order of the expected extent of decarboxylation.

We also obtained difference spectra comparing the acetylated samples with the as-received coals. In some of Paul Painter's work he has claimed that the asymmetry of the acetate feature around 1760-1780 cm^{-1} has a contribution from alcoholic acetate centred at 1740 cm^{-1} I feel that the origin of the asymmetry is a combination of the liberation of carboxylic acid functions and a change in the nature of their hydrogen-bonding environment.
The difference spectra are indexed as ACETxxxx where xxxx is the spectrum number above. Again the energy ordinate (peak height of the acetate carbonyl absorption) gives meaningful information:

0.1935 ACET5718 (P-668)
0.3088 ACET5729 (84-138)
0.3447 ACET5751 (84-139)
0.3188 ACET5730 (84-140)
0.3596 ACET5720 (84-141)
0.3607 ACET5731 (84-142)

The energy ordinate is proportional to the weight concentration of acetate groups, which is (naturally) lower for the original coal with its appreciable carboxyl group content.
The corresponding differences for the demineralised samples are:

0.1918 ACET5747 (P668)
0.2666 ACET5748 (84-138)
0.3271 ACET5750 (84-141)
0.3449 ACET5749 (84-142)

If spectra ACET5747 and ACET5718 are compared, the point suggested above (that asymmetry in the acetate carbonyl band of a difference spectrum indicates differences in the carboxylic/carboxylate proportions) is neatly confirmed: there is little asymmetry in ACET5747.
Another remarkable feature shows up in the difference spectrum ACET5748, for the demineralized 84-138 sample. This is the most extensively decarboxylated, and appears to have undergone a fair amount of C-acetylation (this is not without precedent for the acetylating conditions we have used); it is to be expected since the deactivating influence of carboxyl functions has been removed.

TABLE 4

Interim report, 1985 January 24, continued

Dr. J. A. MacPhee Page 3

To summarize briefly, the major changes occurring on processing the lignite are decarboxylation, and modification of the mineral content for the more drastically heated samples.

I trust that this information is useful in characterizing the samples, and in demonstrating what can be achieved through a combination of PA-FTIR spectroscopy and chemical manipulation.

We have almost completed the series of demineralization experiments on the asphaltene samples you sent recently. I will send them along as soon as we get a chance to plot them out and compose a commentary.

I would like to raise the question of prospects for a "Phase III" of this work, since the end of the present contract is approaching, and we do not have any new prospects at the moment other than the application for an E M & R Research Agreement (I left a copy with you on my last visit to Ottawa). Perhaps we can discuss this point when we next talk on the telephone.

Yours sincerely,

Brian

Brian Lynch
Professor & Chairman, Department of Chemistry

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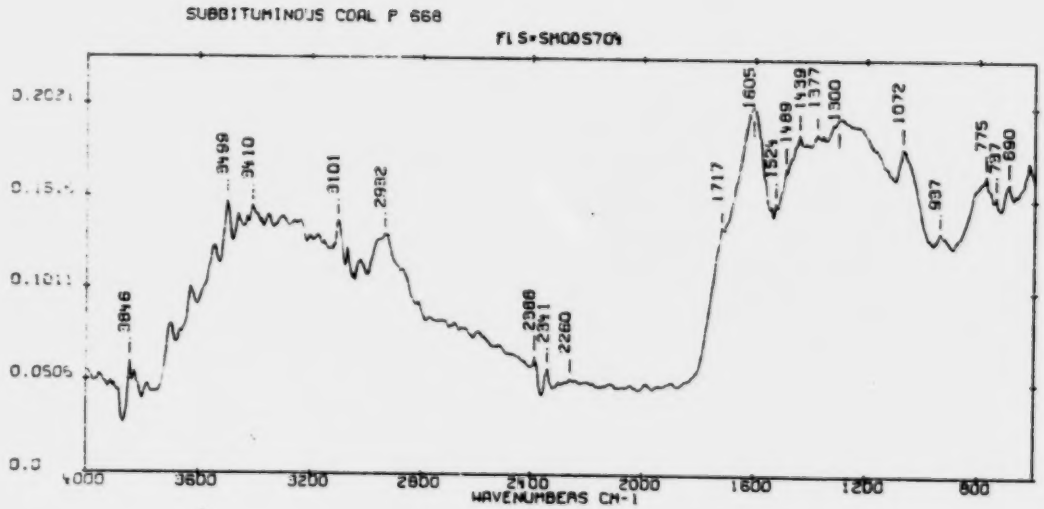
FIGURE 25

SUB-BITUMINOUS COAL P-668



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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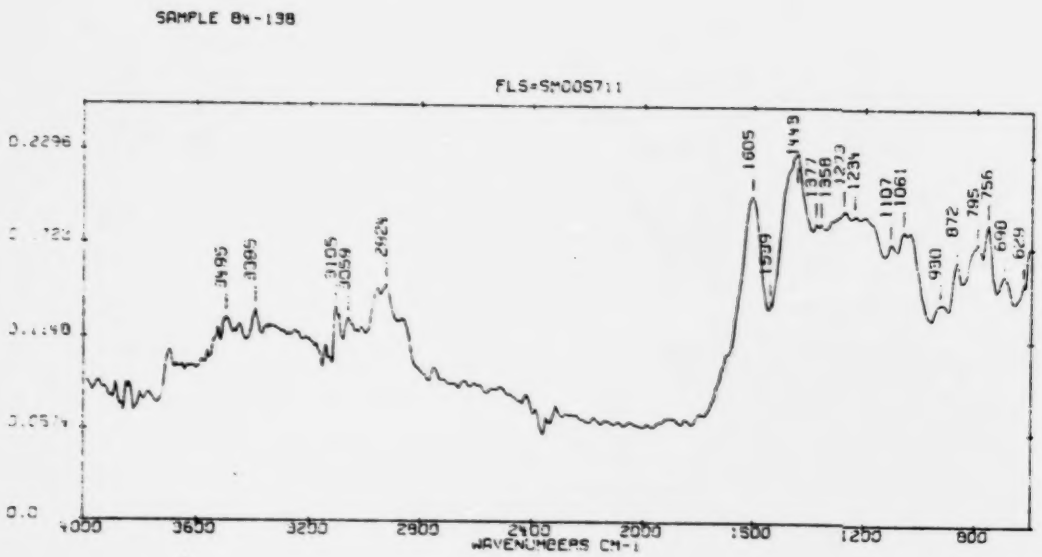
FIGURE 26

SAMPLE 84-138

P-668 heated 1 h at 400°C

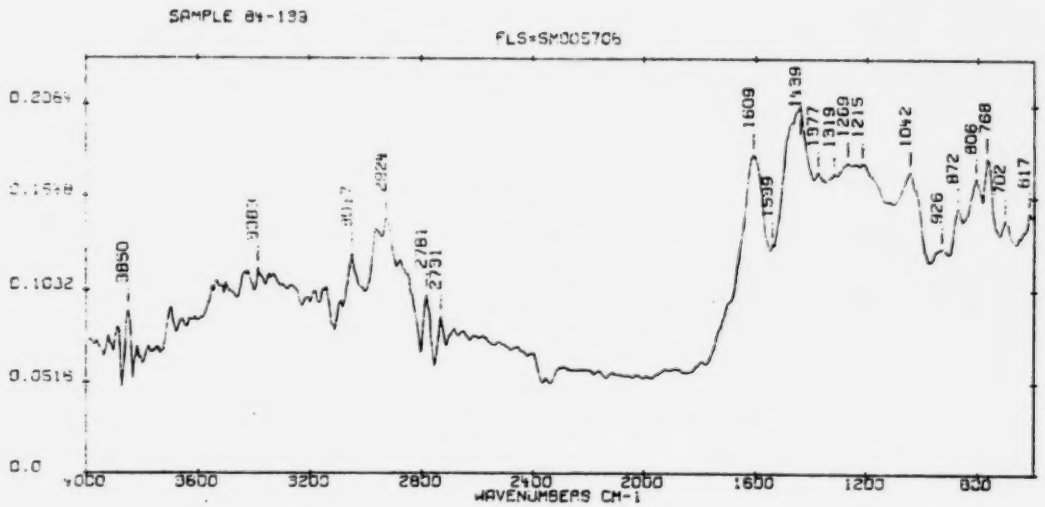


PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FIGURE 27

SAMPLE 84-139

P-668 heated 2 h at 375°C

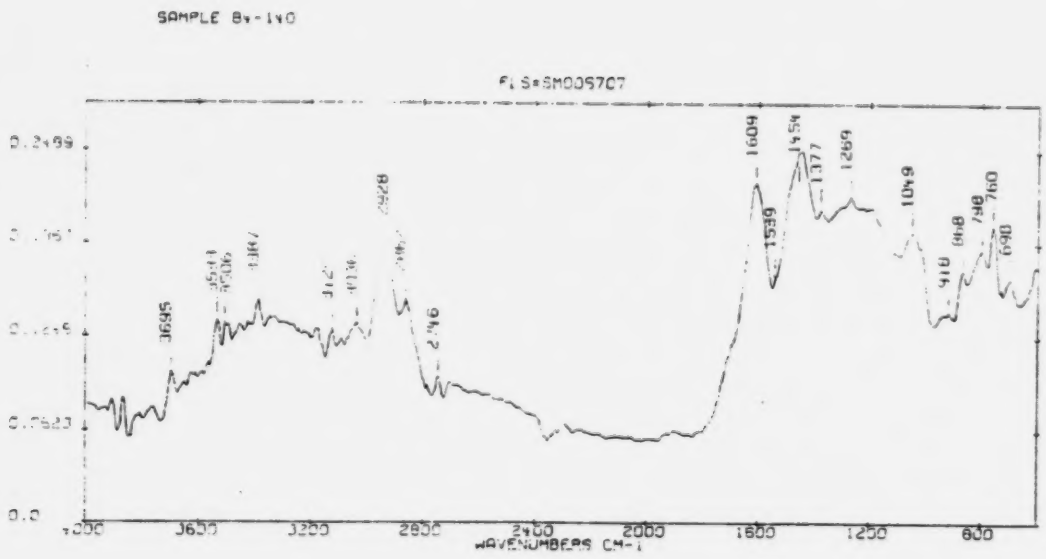


PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FIGURE 28

SAMPLE 84-140

P-668 heated 2 h at 360°C

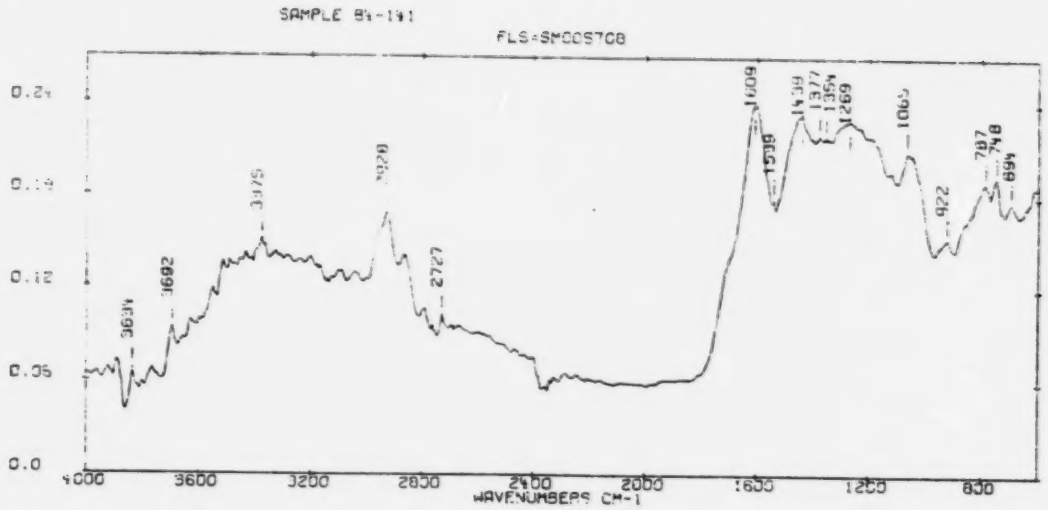


37

FIGURE 29

SAMPLE 84-141

P-668 heated 0.3 h at 360°C

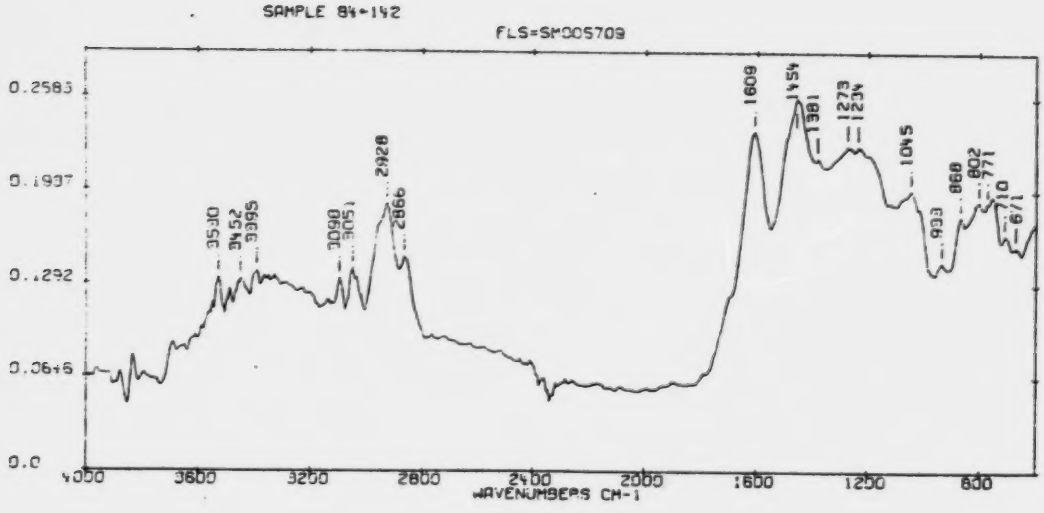


PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FIGURE 30

SAMPLE 84-142

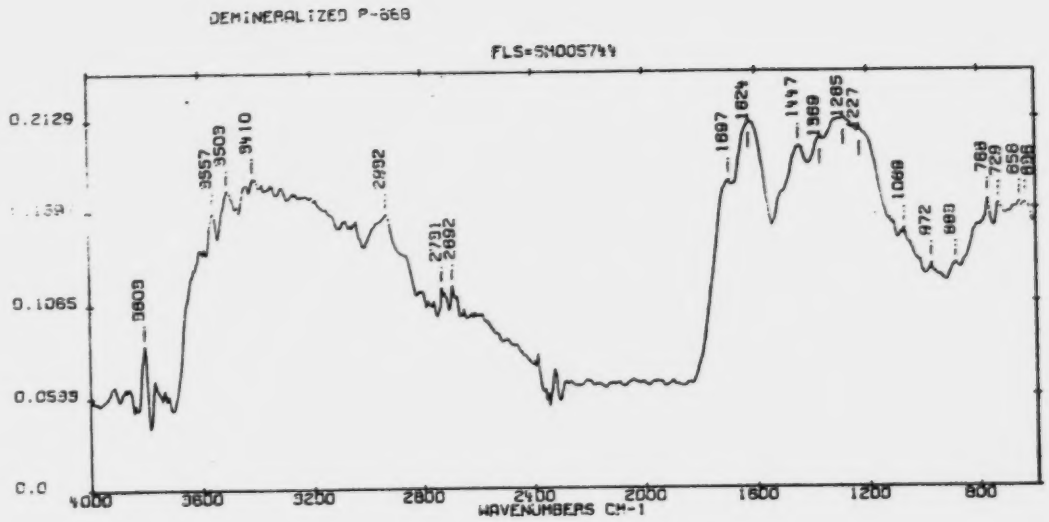
P-668 heated 2 h at 345°C



39

FIGURE 31

P-668 DEMINERALIZED



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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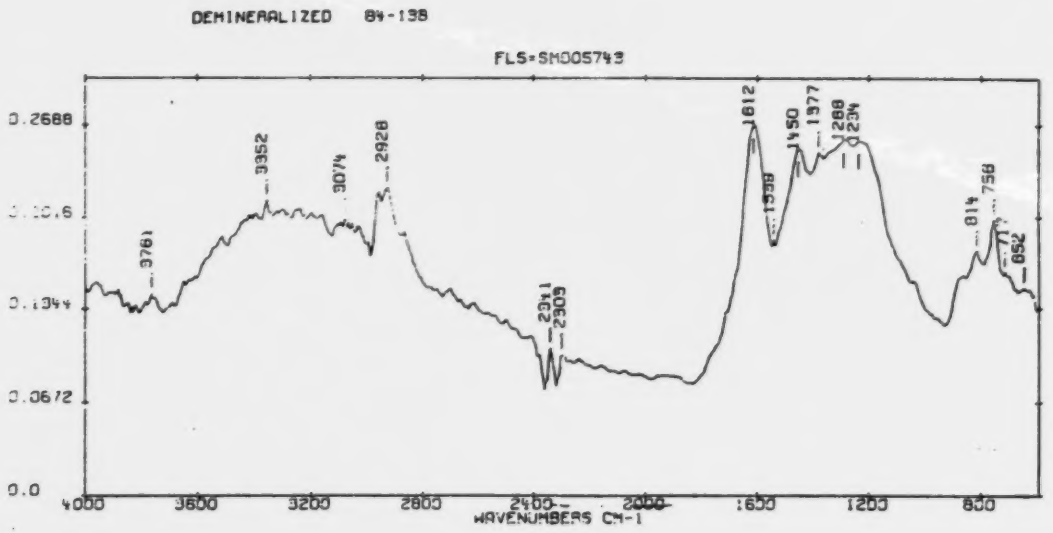
FIGURE 32

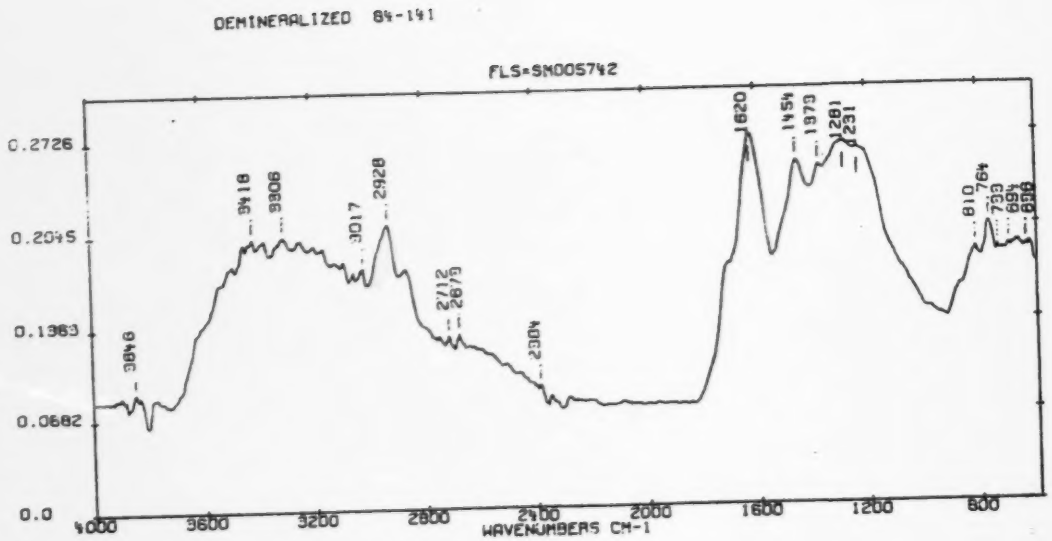
84-138 DEMINERALIZED



41

FIGURE 33

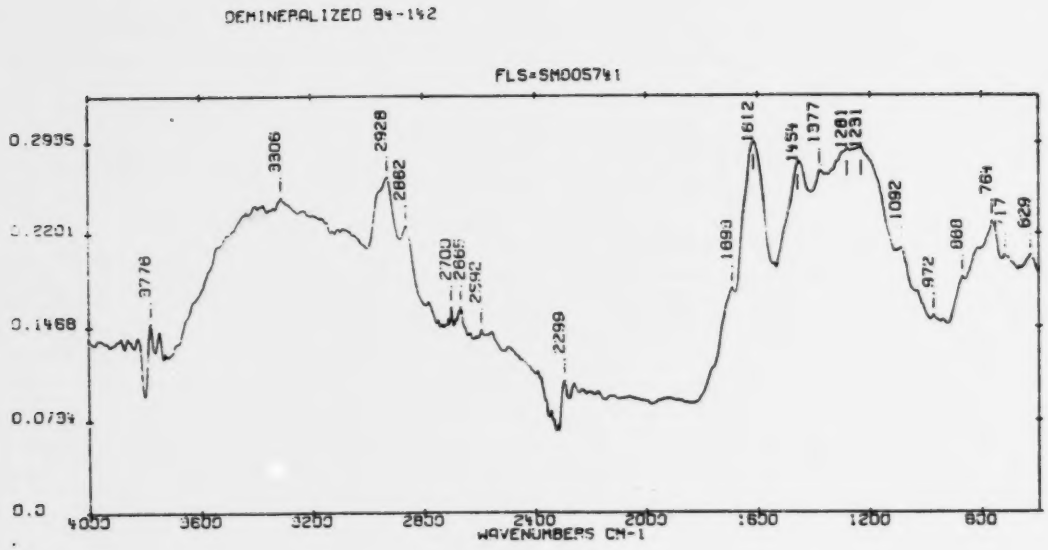
84-141 DEMINERALIZED



42

FIGURE 34

84-142 DEMINERALIZED



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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FIGURE 35

ACETYLATED P-668

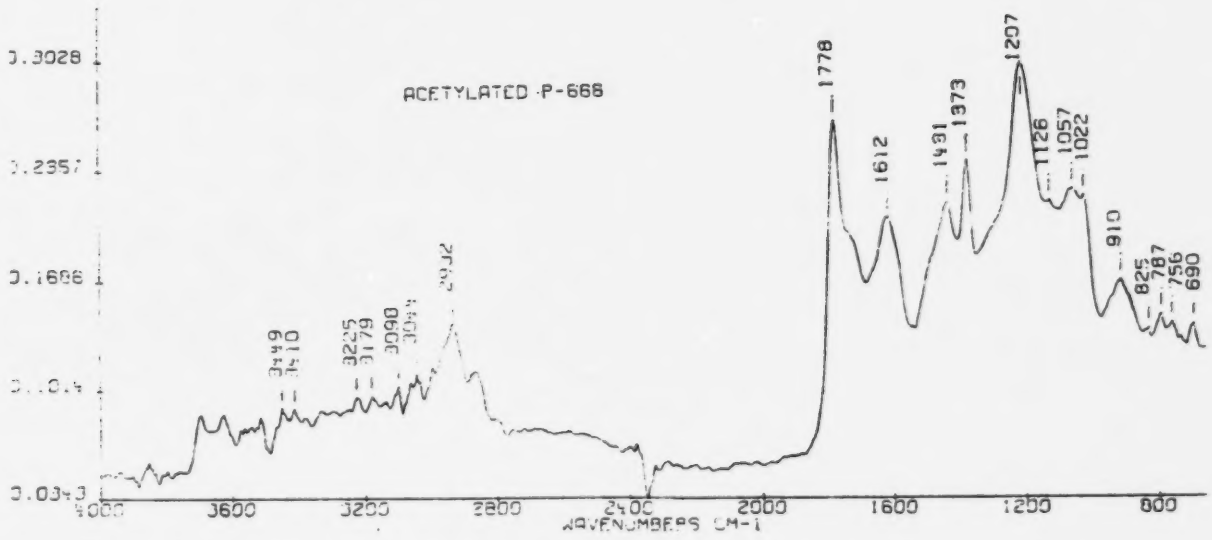
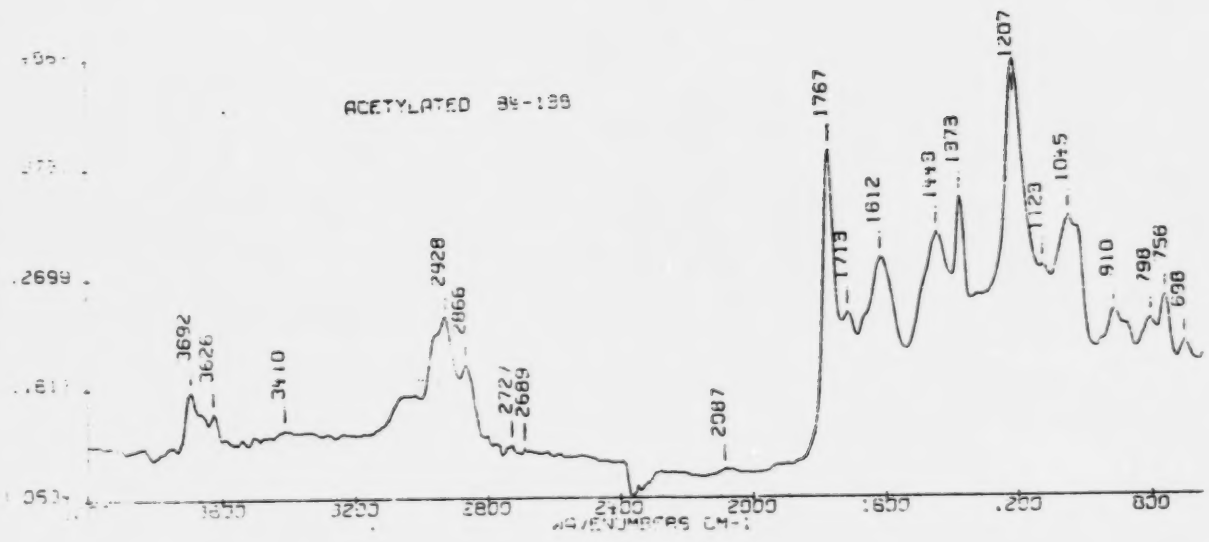
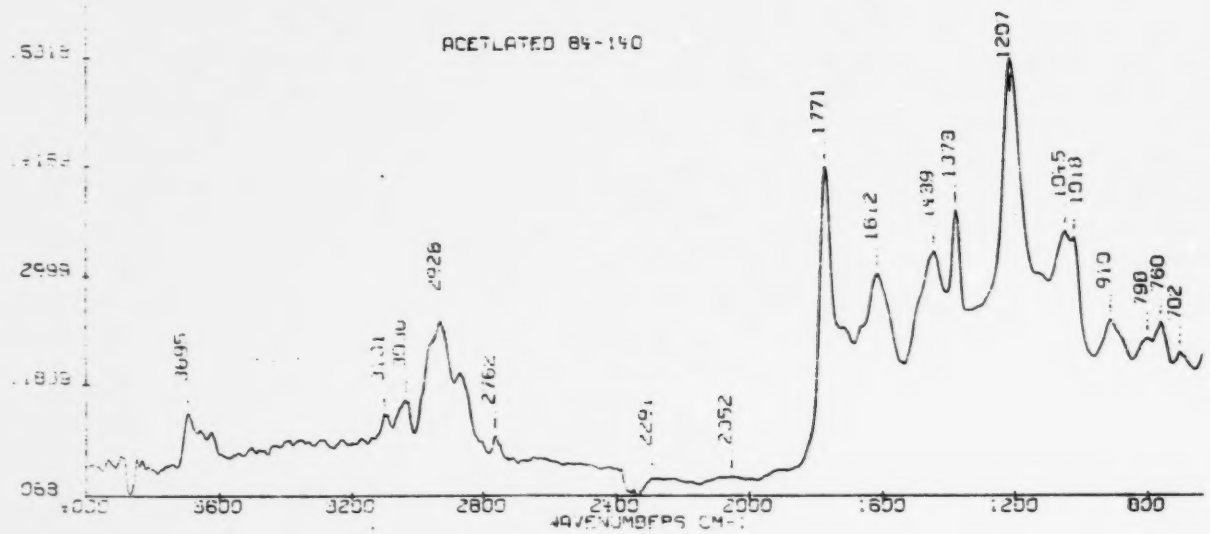


FIGURE 36
ACETYLATED 84-138



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

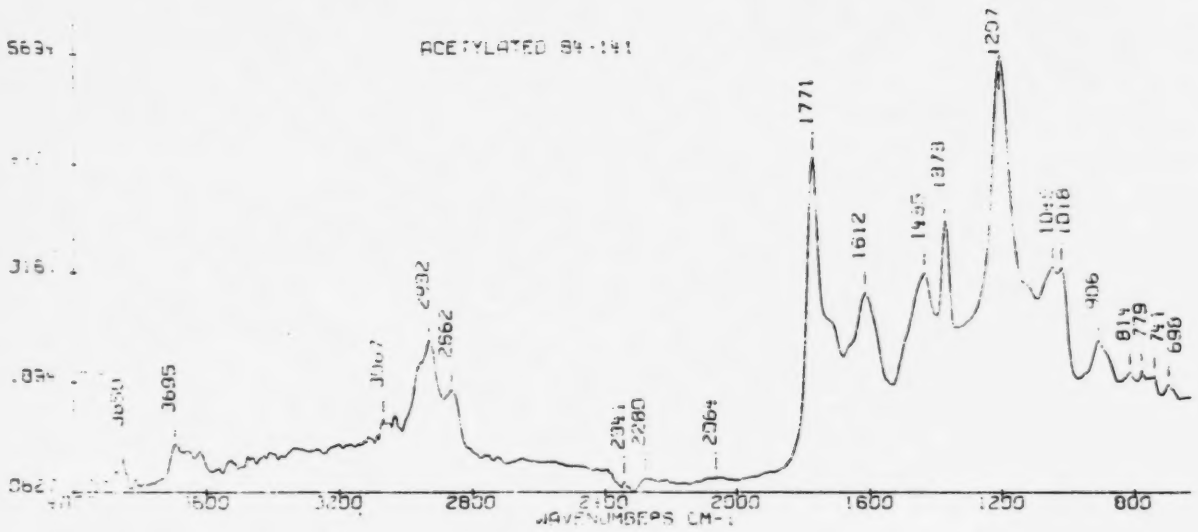
FIGURE 37
ACETYLATED 84-140



46

FIGURE 38

ACETYLATED 84-141



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

FIGURE 39

ACETYLATED 84-142

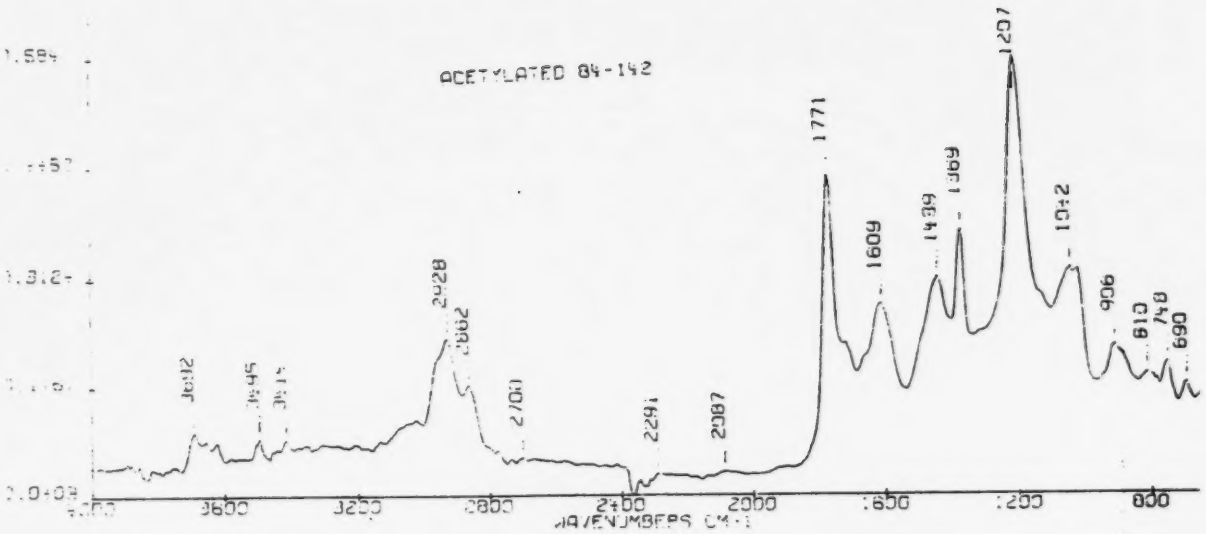


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FIGURE 40

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
DEMINERALIZED P-668 minus DEMINERALIZED 84-138

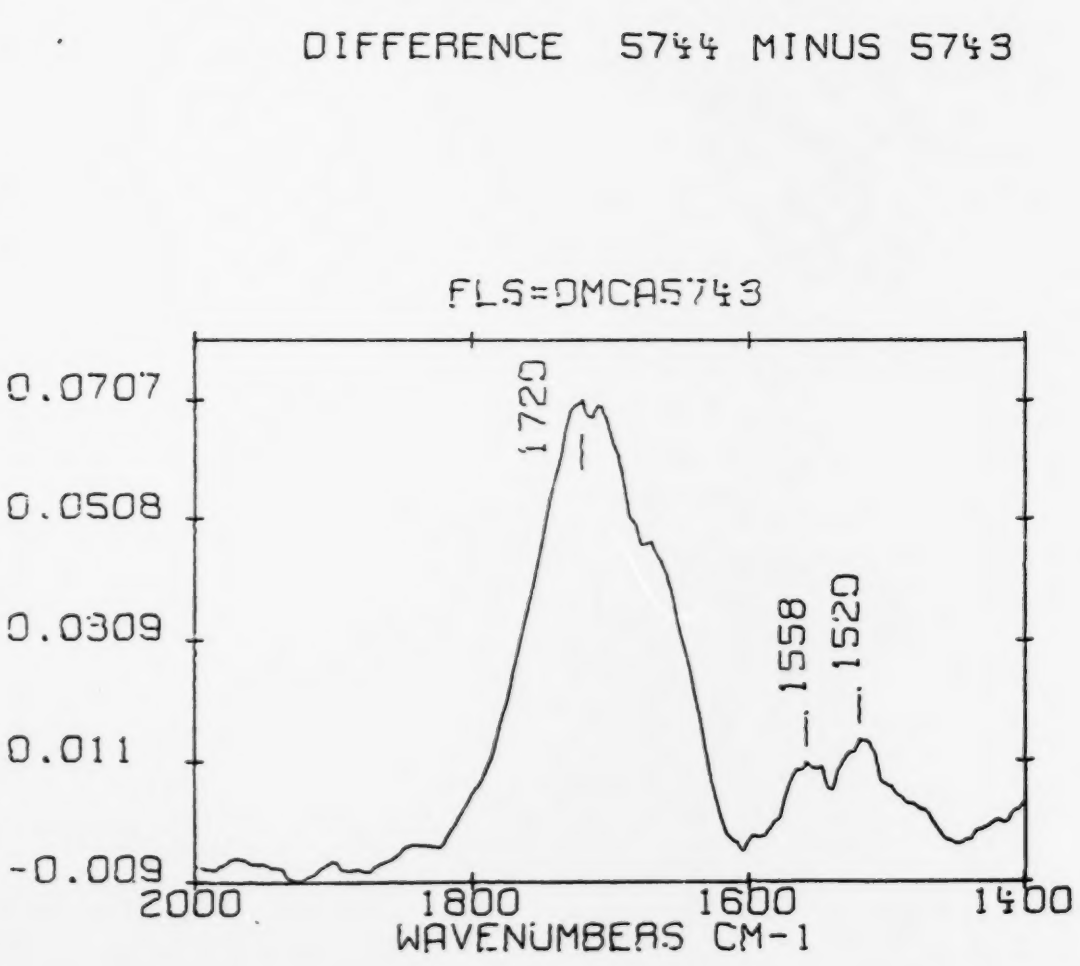
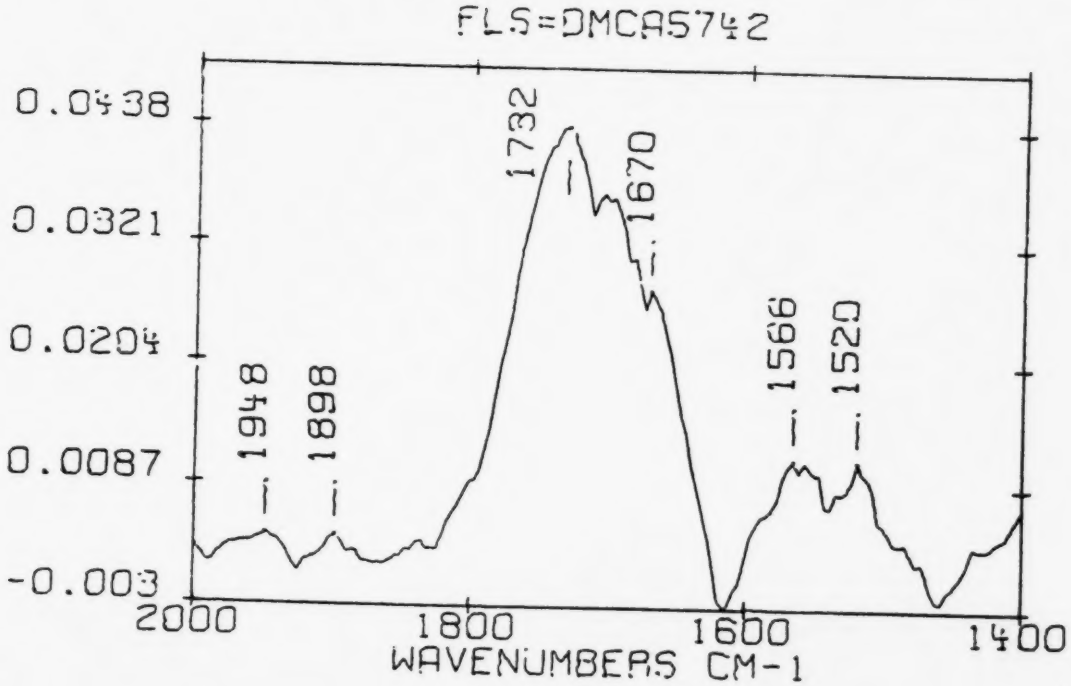


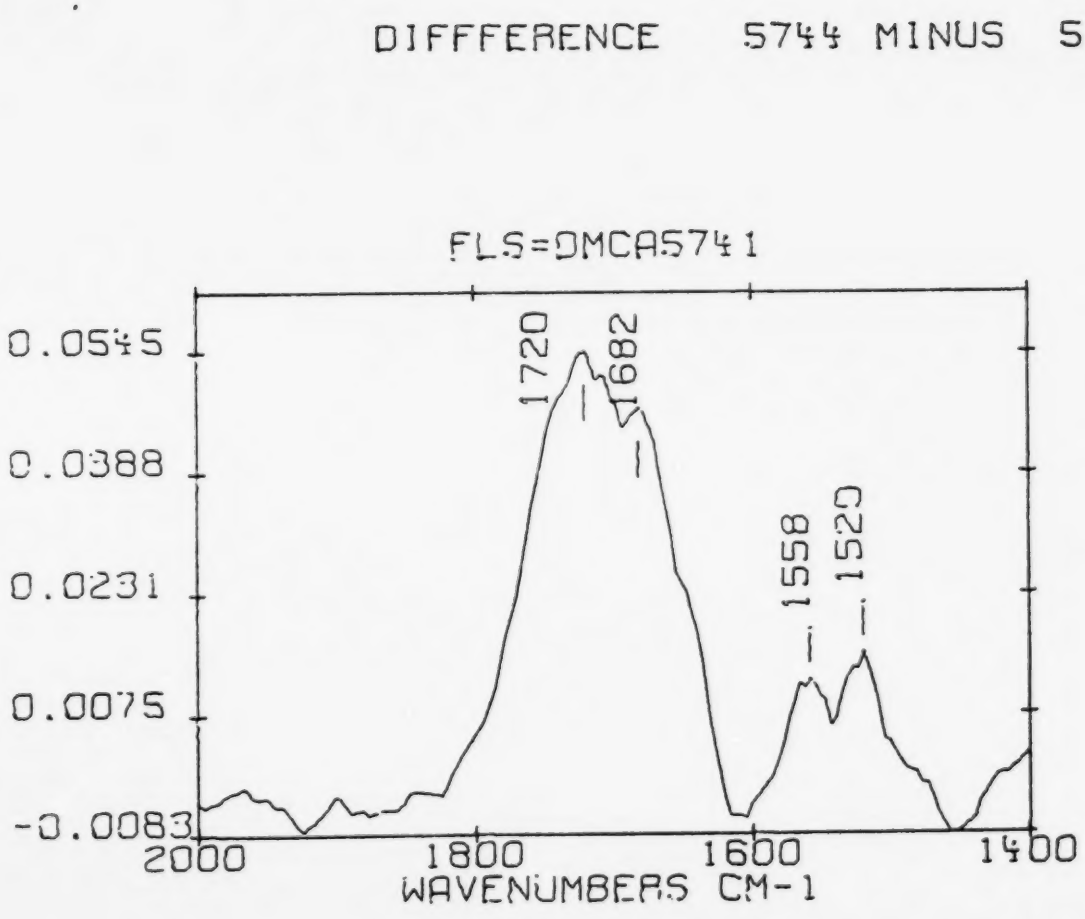
FIGURE 41
DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
DEMINERALIZED P-668 minus DEMINERALIZED 84-141



50

FIGURE 42

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
DEMINERALIZED P-668 minus DEMINERALIZED 84-142



51

FIGURE 43

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED P-668 minus P-668 AS RECEIVED

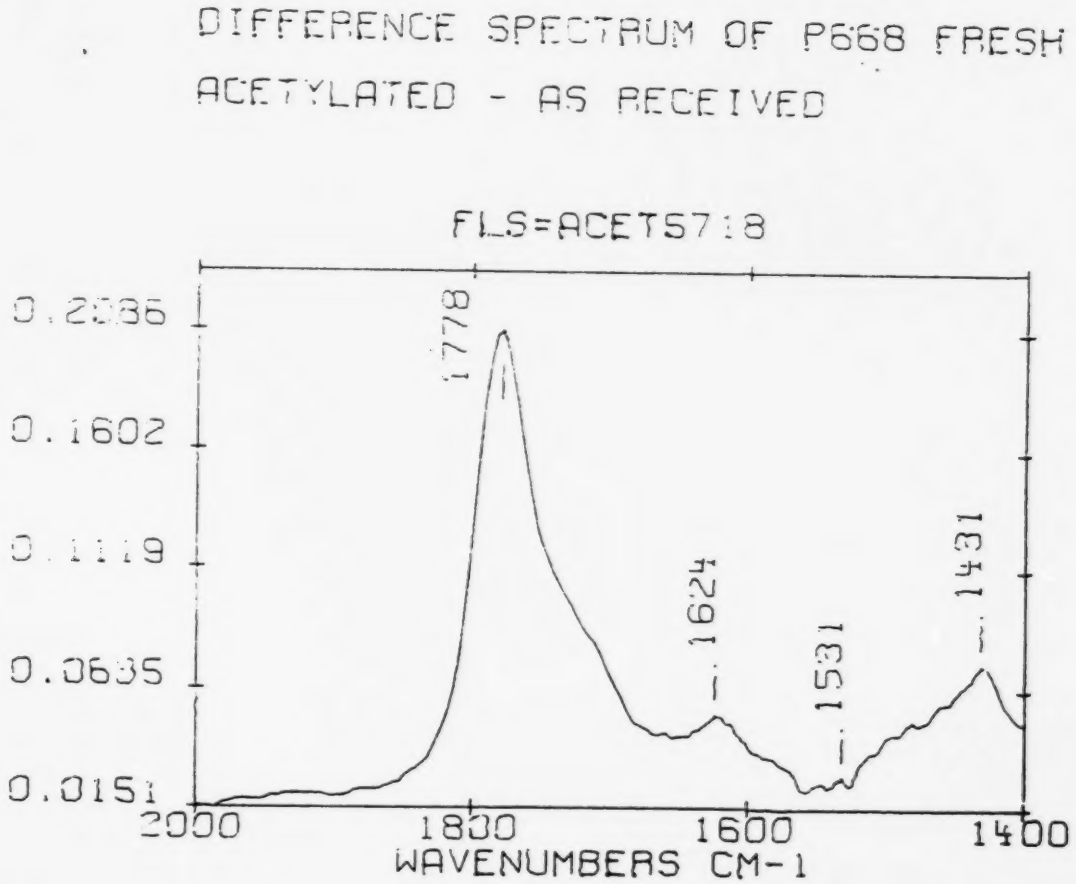


FIGURE 44
DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED 84-138 minus 84-138 AS RECEIVED

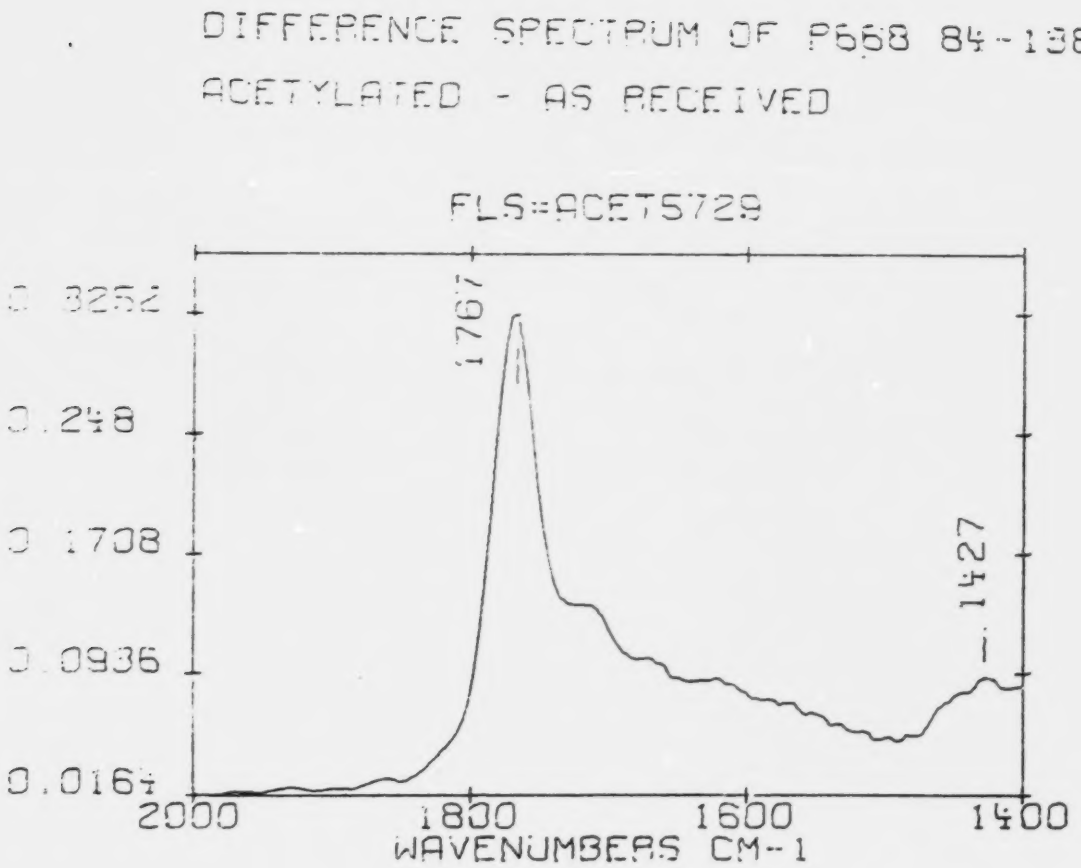
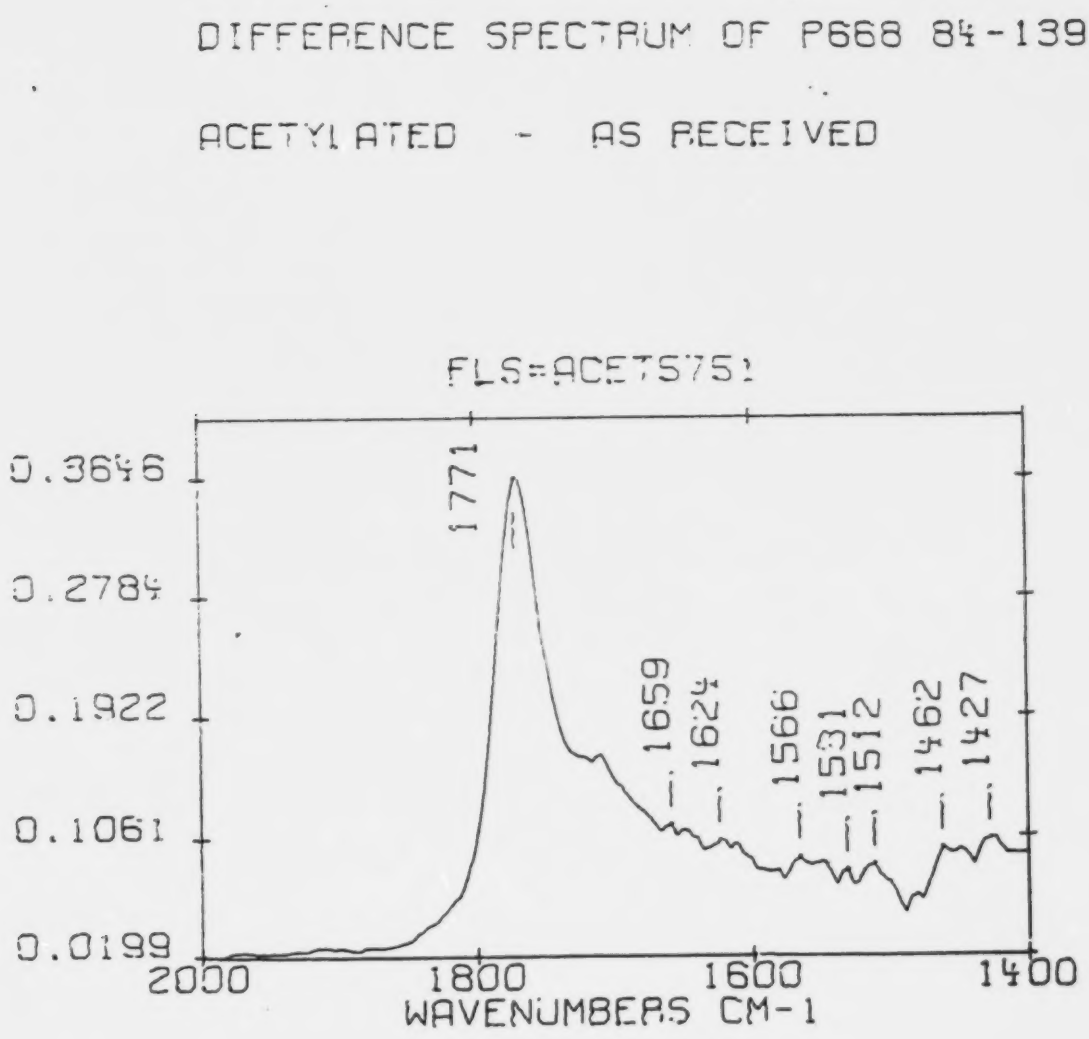


FIGURE 45
DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED 84-139 minus 84-139 AS RECEIVED



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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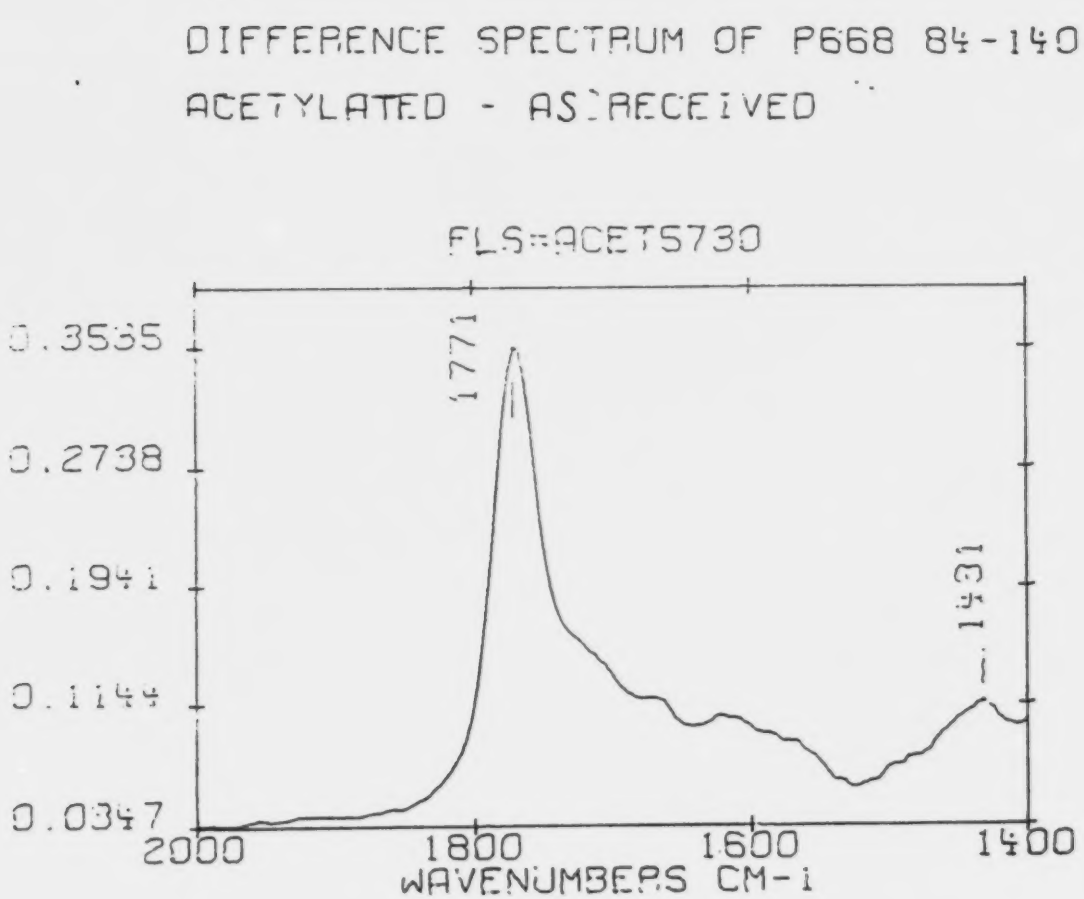
FIGURE 46
DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED 84-140 minus 84-140 AS RECEIVED

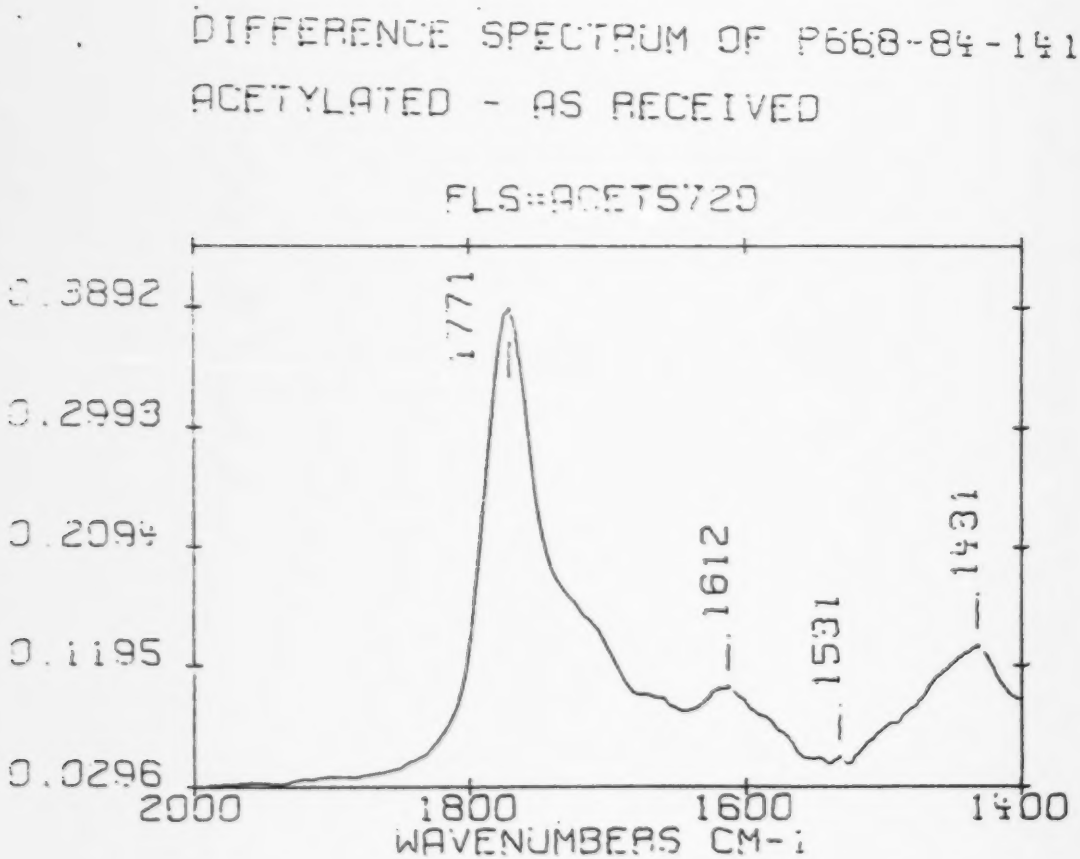


84-141

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

55

FIGURE 47
DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED 84-141 minus 84-141 AS RECEIVED



56

FIGURE 48

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED 84-142 minus 84-142 AS RECEIVED

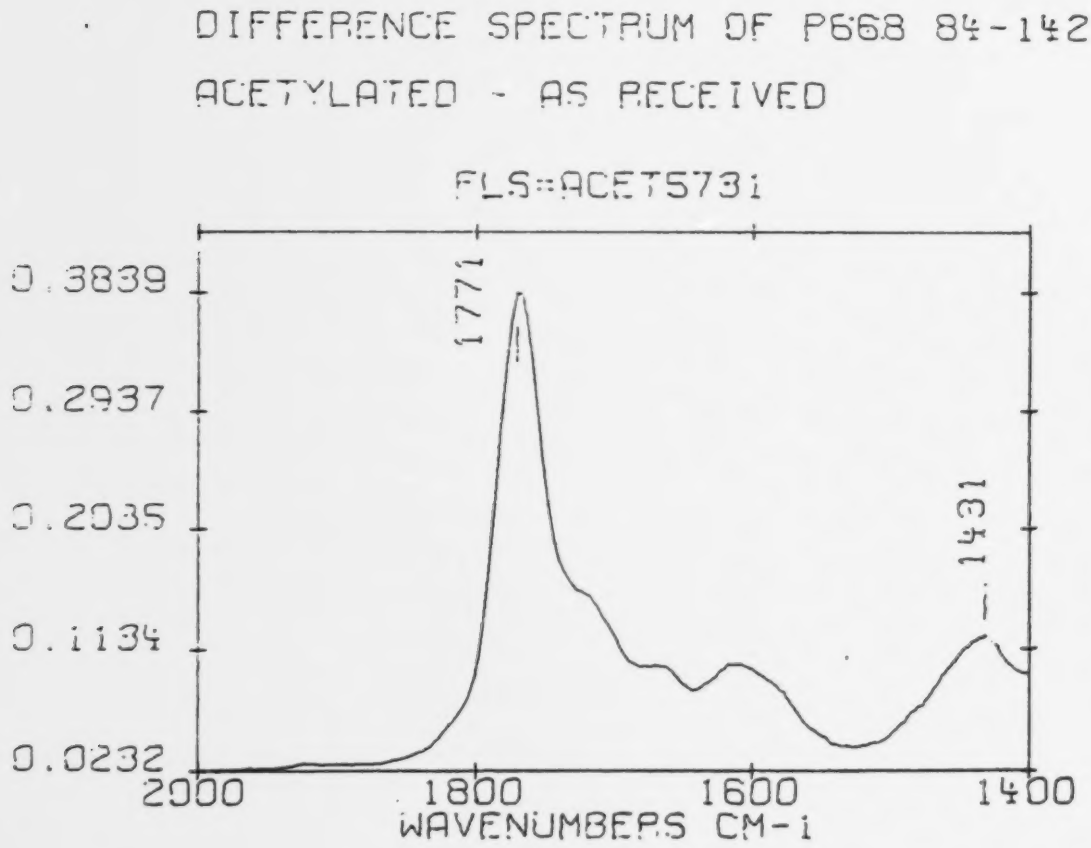


FIGURE 49

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED DEMINERALIZED P-668 minus DEMINERALIZED P-668

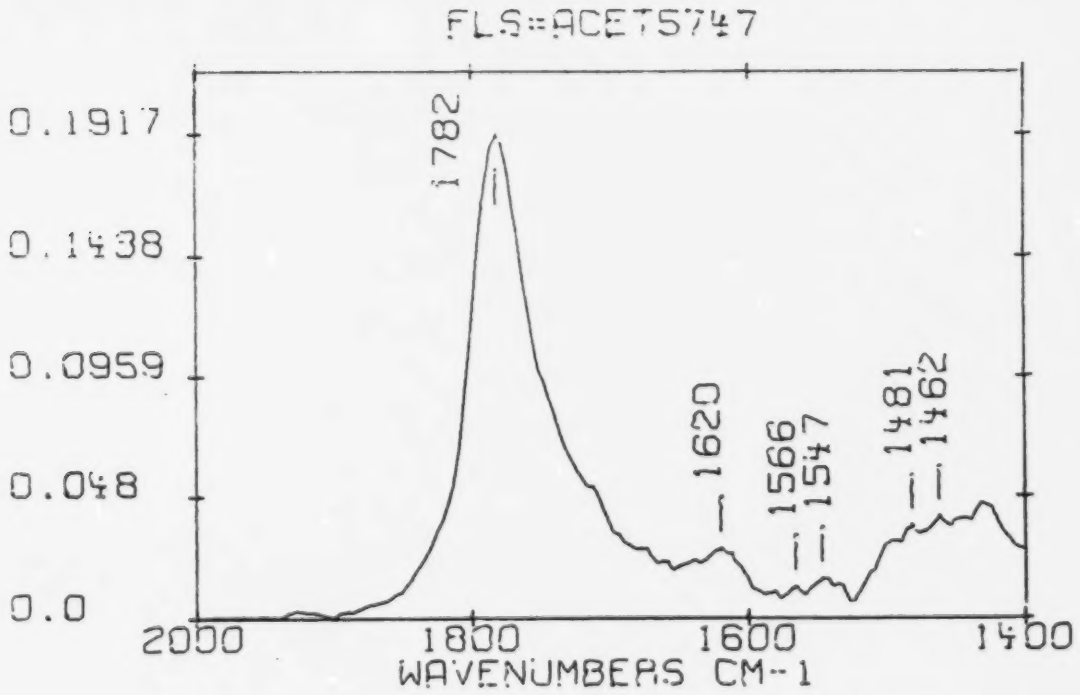


FIGURE 50

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED DEMINERALIZED 84-138 minus DEMINERALIZED 84-138

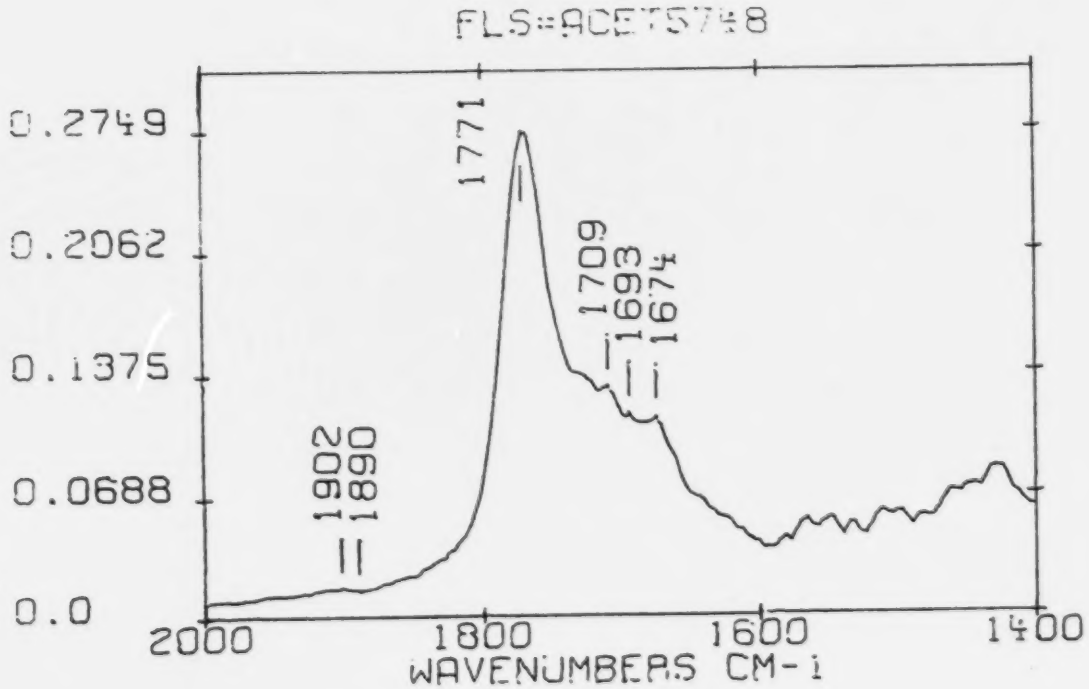
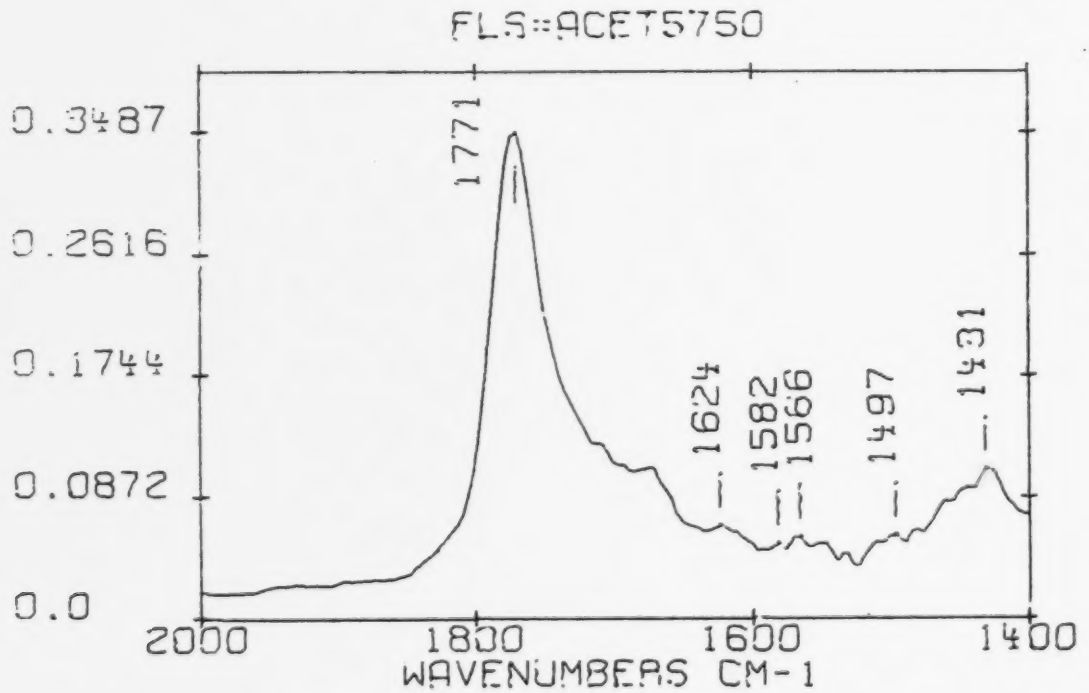


FIGURE 51

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),

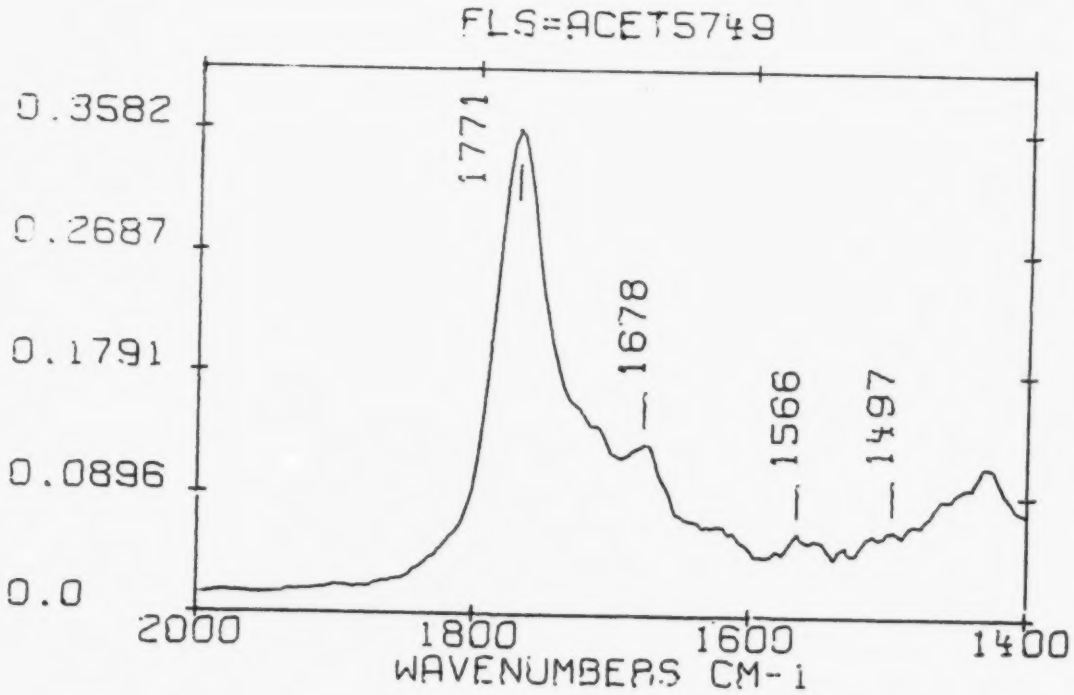
ACETYLATED DEMINERALIZED 84-141 minus DEMINERALZED 84-141



60

FIGURE 52

DIFFERENCE SPECTRUM (2000-1400 CM^{-1}),
ACETYLATED DEMINERALIZED 84-142 minus DEMINERALIZED 84-142



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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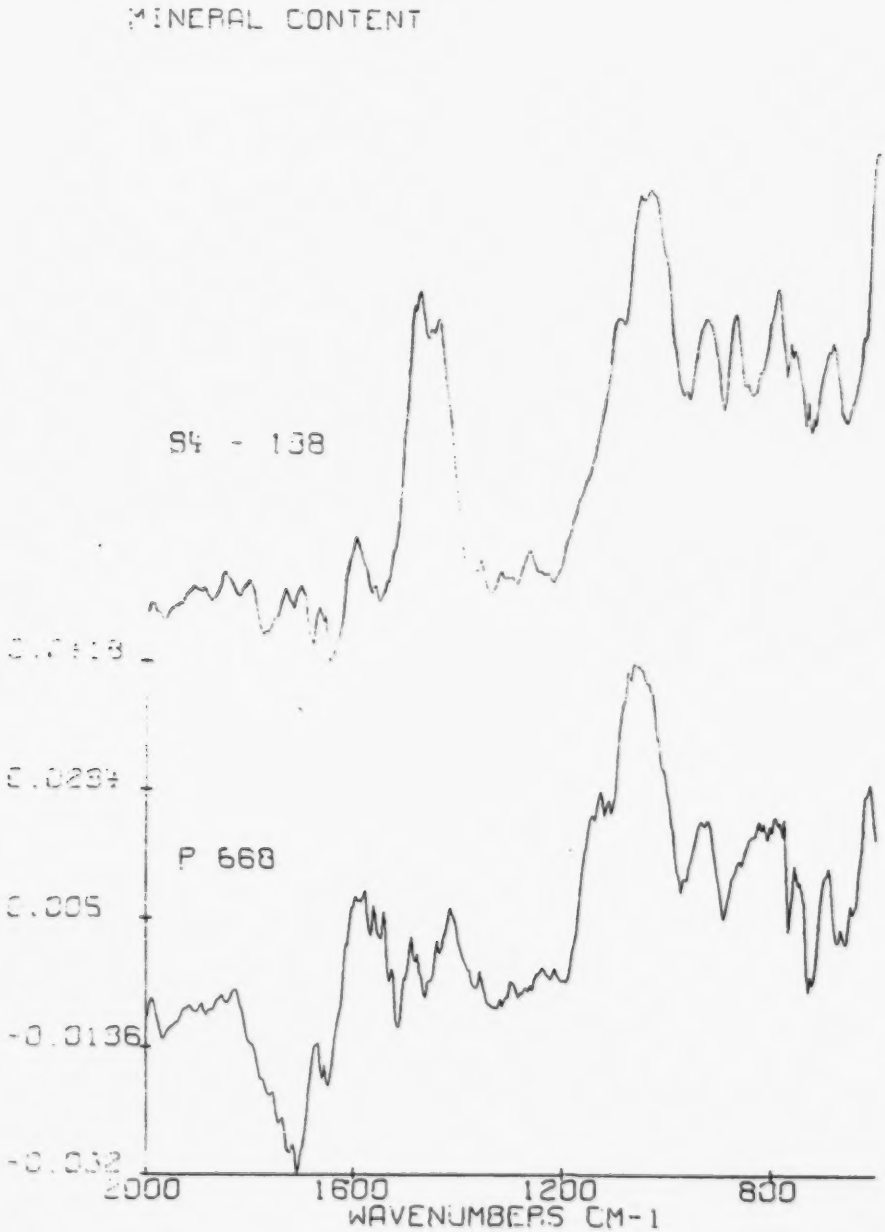
FIGURE 53

MINERAL CONTENT IN 84-138 AND P-668 SAMPLES

(from spectral subtraction of demineralized from as-received samples)



62

ASPHALTENES DERIVED FROM TAR-SANDS BITUMENS, SUBJECTED TO DEMINERALIZATION TREATMENTS

The samples subjected to spectroscopic examination are described in the incorporated interim reports of 1985 February 11 and March 11, indexed as Tables 5-7.

The spectra referred to are reproduced as Figures, commencing with Figure 54.

TABLE 5

Interim report, 1985 February 11

1985 February 11

Dr. J. A. MacPhee
Research Scientist
CANMET/Energy Research Laboratories
Energy, Mines, and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1

Dear Tony:

I enclose copies of PAIFT spectra for the various asphaltenes derived from the oil-sands bitumens subjected to various treatments and also subjected to standard chemical demineralization procedures.

The samples included asphaltenes from the following sources:

1. Athabasca bitumen
2. Cold Lake (cold-bailed) bitumen
3. Shaker Run 83-112
4. Hydrogenated Athabasca bitumen
5. Cold Lake bitumen
6. Hydrogenated Cold Lake bitumen

All the asphaltene samples apart from # 6 are changed appreciably by the demineralization treatments, in the sense that characteristic absorptions from kaolinite/illite-type (in the 1100-1000 cm^{-1} region) and quartz-type (in the 800 cm^{-1} region) minerals are removed from the spectra of the demineralized samples.
Sample # 6 gave weak indications of mineral-matter and was almost unchanged by the demineralization treatment.

Most of the as-received asphaltenes are essentially demineralized by one pass (successive treatments with refluxing HCl, 1:1 HF at 50-55°C, and again with HCl), but sample #2 (the cold-bailed material) required three successive treatments before the contaminating minerals were judged to be absent. I presume that the asphaltene from the cold-bailed material remains substantially more viscous than the asphaltene from the conventionally isolated bitumen, so that penetration of the demineralizing acid species is less efficient.
The composition (and the relative amounts) of the minerals extracted from the asphaltenes may be deduced from the difference spectra, i.e.i

(as-received spectrum) minus (demineralized spectrum)

where a least-squares procedure is used to minimize the differences between the two spectra.

TABLE 6

Interim report, 1985 February 11, continued

The sheet with five plots labelled as MINERAL1 through MINERAL5 illustrates the compositional differences - note that the as recieved Athabasca sample contains little quartz absorption (MINERAL1) while the material from the hydrogenated bitumen (MINERAL4) has undergone dehydration during the processing. Also, the proportion of quartz in the Cold Lake - derived species is greater for the conventionally processed material than for the cold-bailed, and the amount of total mineral is greater with the cold-bailed material. The presence of mineral-matter absorption in the 1000 cm^{-1} region has little influence on any other absorptions, but the quartz-derived feature around 800 cm^{-1} renders risky any conclusions about the distribution of aromatic C-H functions in samples which have not been demineralized. I will analyze the results a little further through expanded displays of the 900-600 cm^{-1} region and perhaps something worthy of discussion will turn up.

Please give me a call at 902-867-3992 when you and Dr. Nandi have had a chance to consider this information. We will return the suite of samples to you within the next week.

With best wishes,

Yours sincerely,

Brian M Lynch

Brian M. Lynch
Professor & Chairman, Department of Chemistry

enclosures: PAIFT spectra of asphaltenes & demineralziation products

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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TABLE 7

Interim report, 1985 March 11

ST. FRANCIS XAVIER UNIVERSITY
DEPARTMENT OF CHEMISTRY

1985 March 11

Dr. J. A. MacPhee
Research Scientist
CANMET/Energy Research Laboratories
Energy, Mines, and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1

Dear Tony:

I enclose the following PAIFT spectra and difference spectra of several of the asphaltenes, as follows:

1. Demineralized Cold Lake asphaltene
2. As-received Cold-bailed Cold Lake asphaltene
3. Demineralized Cold-bailed Cold Lake asphaltene
4. Cold Lake asphaltenes
   difference spectrum - original minus reactor-treated
   (difference features are positive aliphatic C-H features, and negative 1600, 1200, and 800 cm^{-1} (aromatic and ether)
5. Cold lake cold-bailed asphaltenes
   difference spectrum - original material minus reactor-treated (difference features are qualitatively similar to # 4)
6. Difference of reactor products
   Cold lake conventional minus Cold Lake cold-bailed
   essentially identical (noise variations only)
7. Difference of parent Cold Lake asphaltenes
   cold-bailed material is richer in aliphatic component and poorer in aromatic species - this reflects greater extraction efficiency of the less viscous, aliphtic-rich material during the cold-bailed process.

I trust that these will prove useful for the conference presentation.

With best wishes,

Yours sincerely,

Brian

Brian M. Lynch

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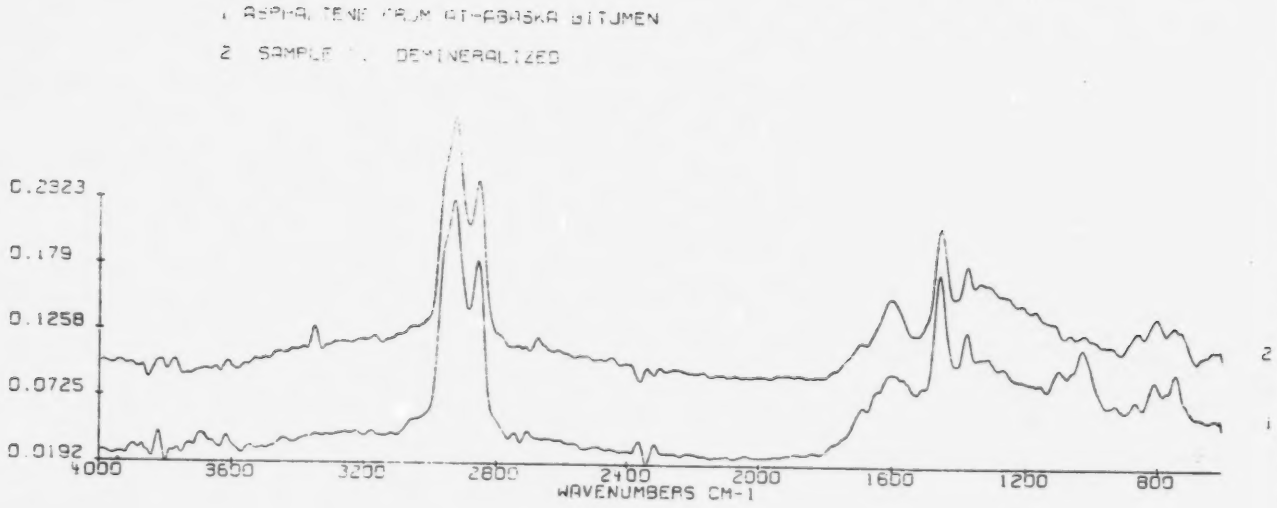
FIGURE 54

1 ASPHALTENE DERIVED FROM ATHABASCA BITUMEN

2 DEMINERALIZATION PRODUCT FROM 1



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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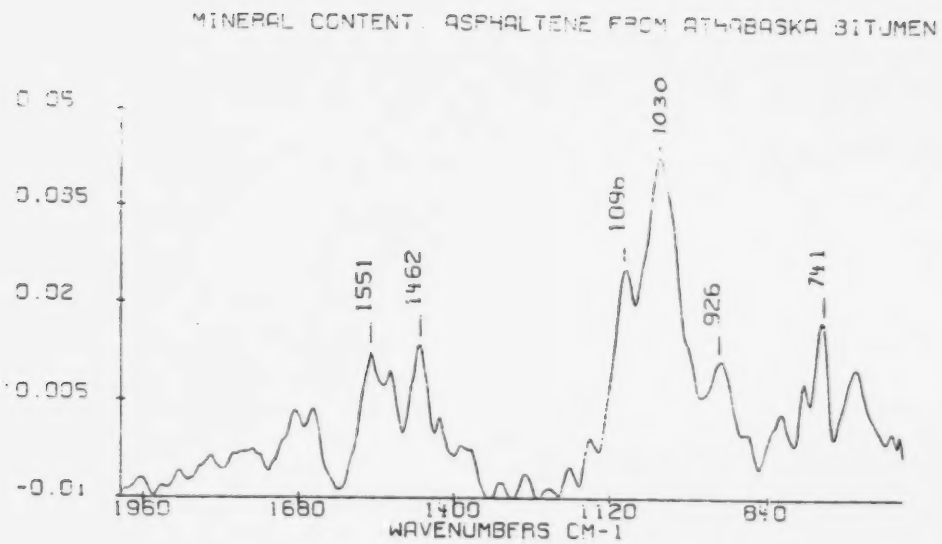
FIGURE 55

MINERAL CONTENT OF ASPHALTENE FROM ATHABASCA BITUMEN

16



68

FIGURE 56

1 ASPHALTENE FROM COLD-BAILED COLD LAKE BITUMEN

2,3 SUCCESSIVE DEMINERALIZATION TREATMENTS WITH HF/HCl

2

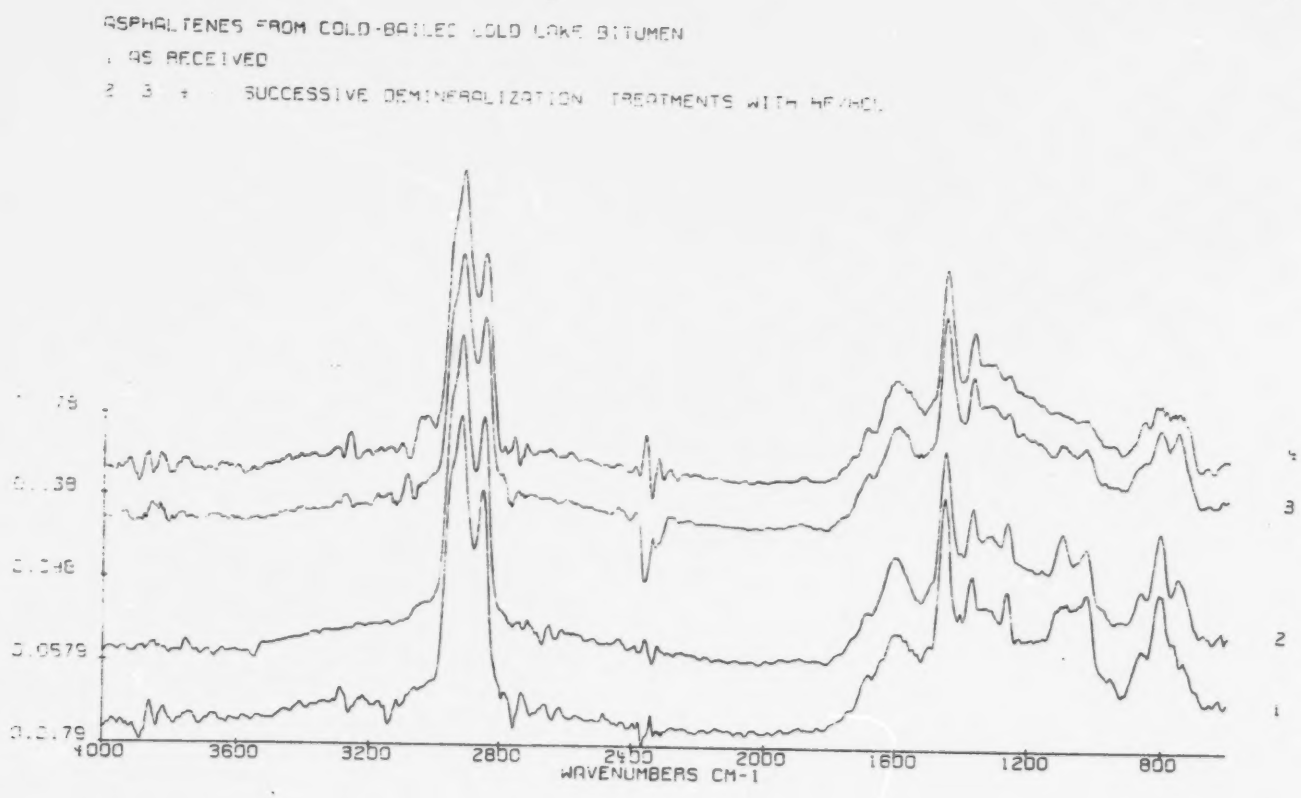


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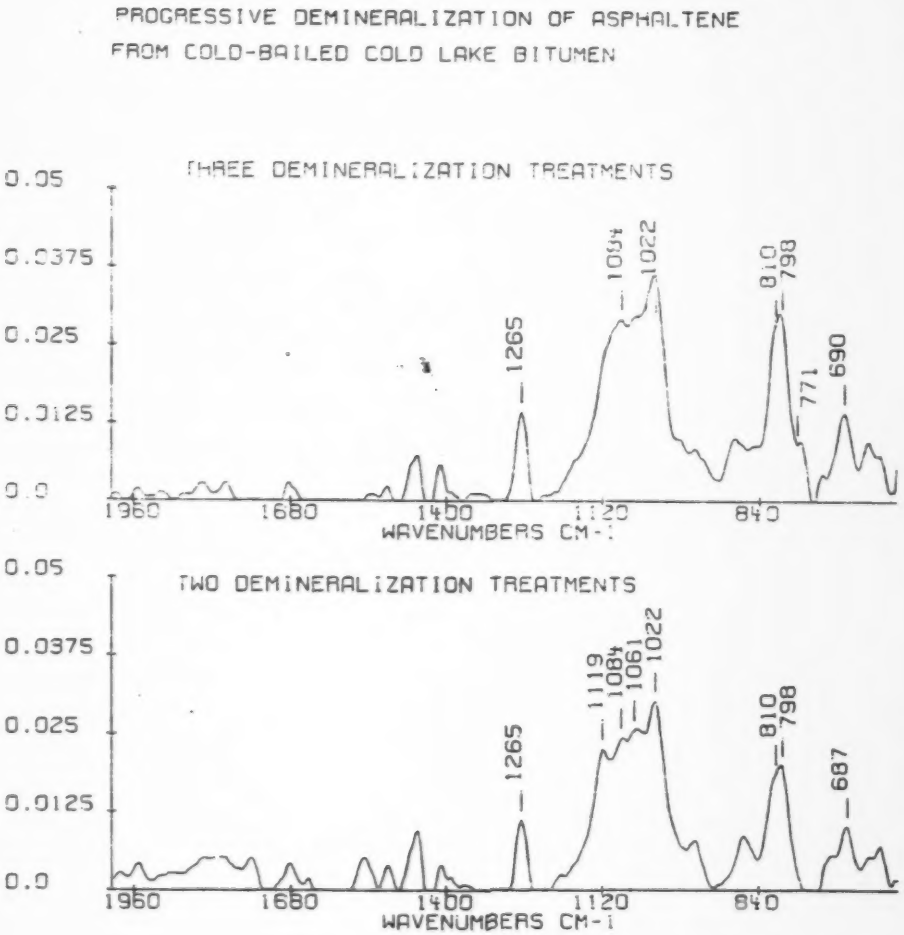
FIGURE 57

MINERAL CONTENT OF ASPHALTENE FROM COLD-BAILED COLD LAKE BITUMEN

2a



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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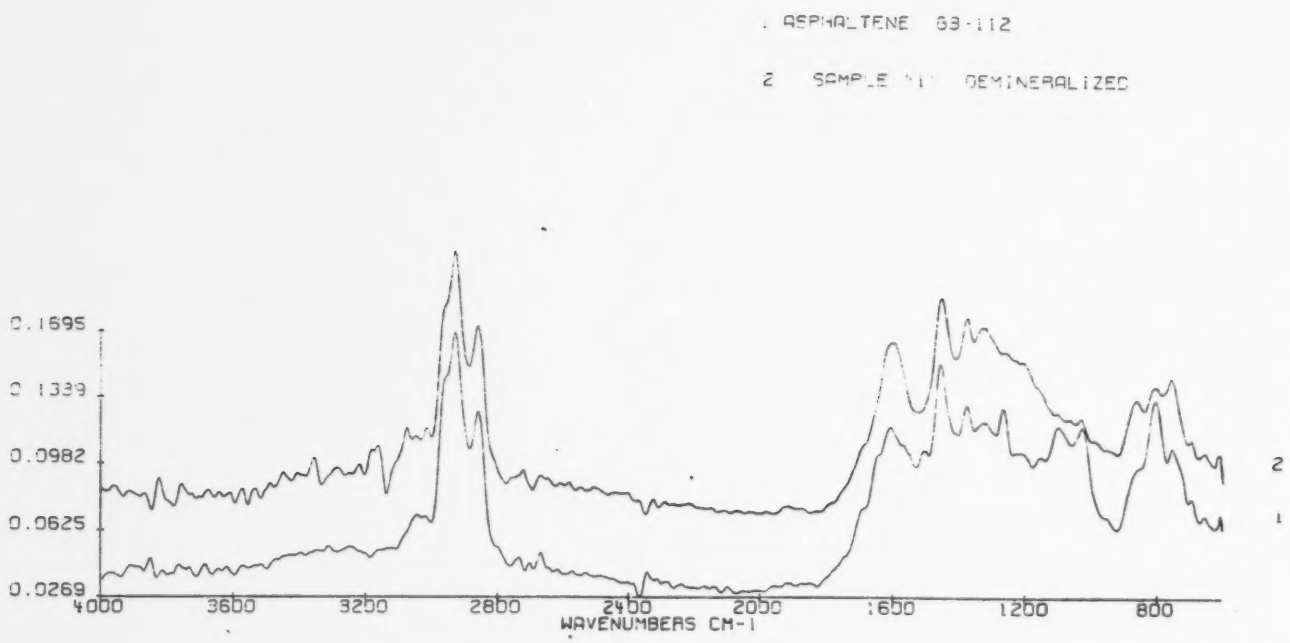
FIGURE 58

1 ASPHALTENE FROM SHAKER RUN 83-112

2 DEMINERALIZATION PRODUCT FROM 1

3 3h

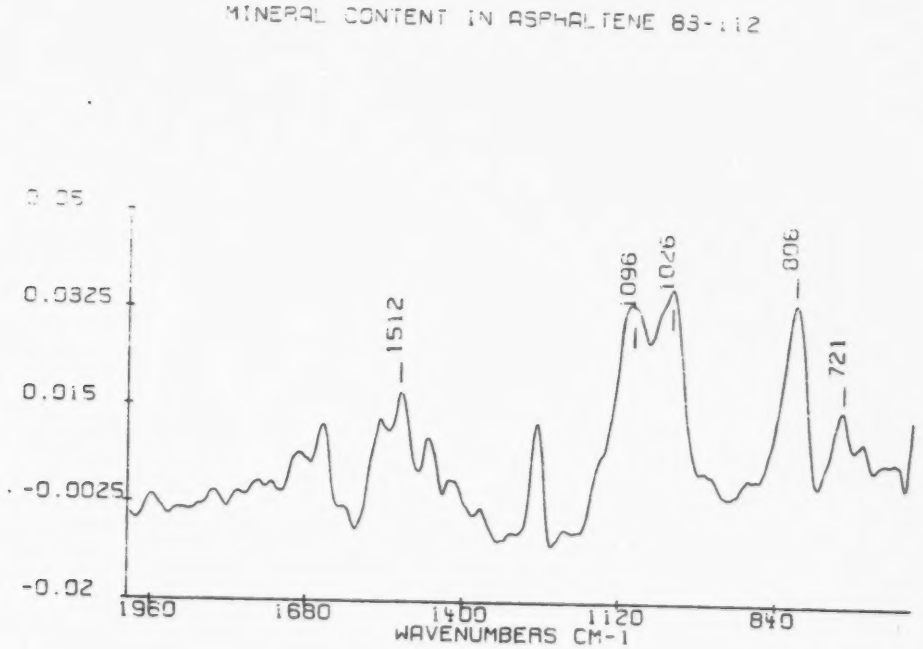


71

FIGURE 59

MINERAL CONTENT IN ASPHALTENE FROM SHAKER RUN 83-112

36



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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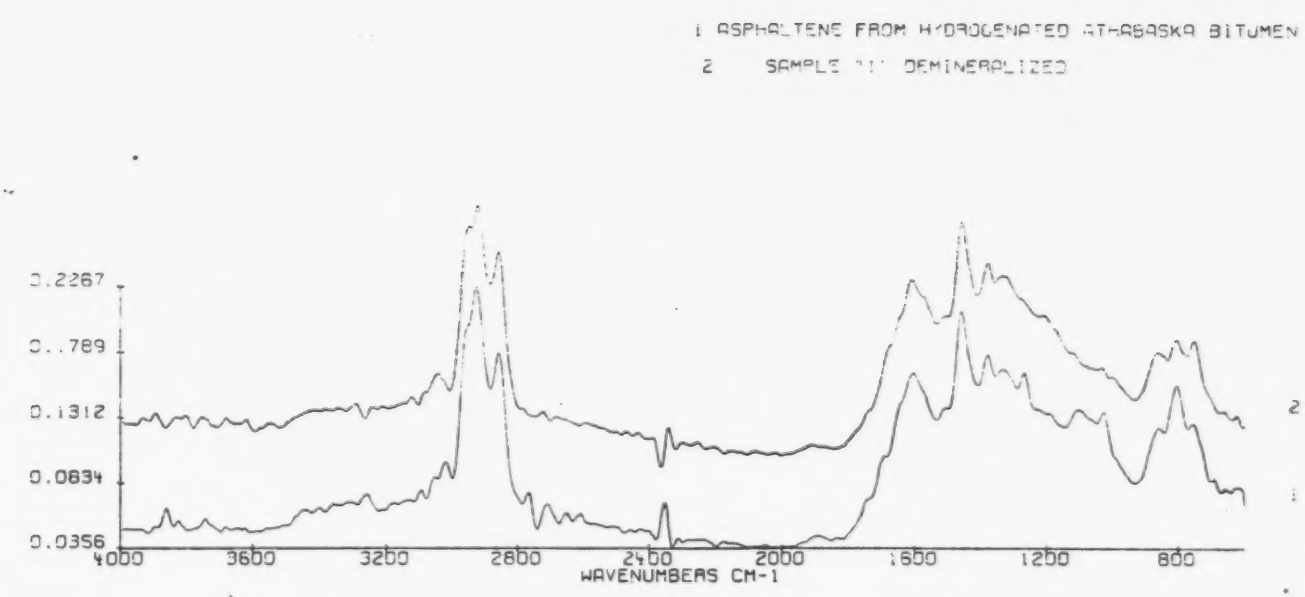
FIGURE 60

1 ASPHALTENE FROM HYDROGENATED ATHABASCA BITUMEN

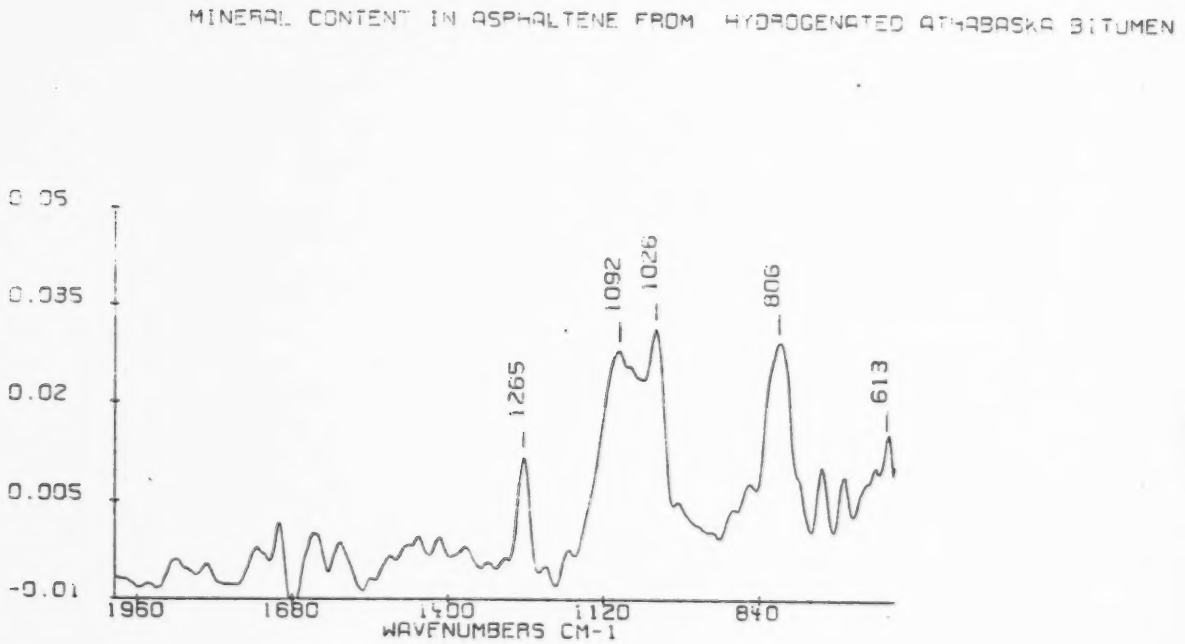
2 DEMINERALIZATION PRODUCT FROM 1



73

FIGURE 61

MINERAL CONTENT IN ASPHALTENE FROM HYDROGENATED ATHABASCA BITUMEN



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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FIGURE 62

1 ASPHALTENE FROM COLD LAKE BITUMEN

2 DEMINERALIZATION PRODUCT FROM 1

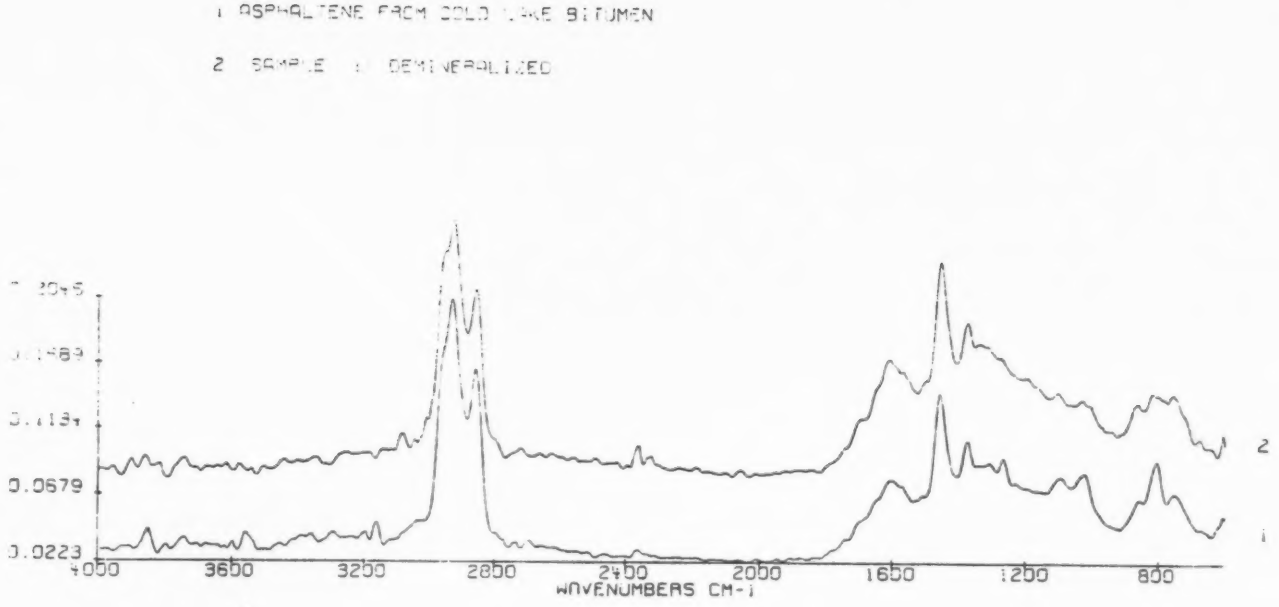
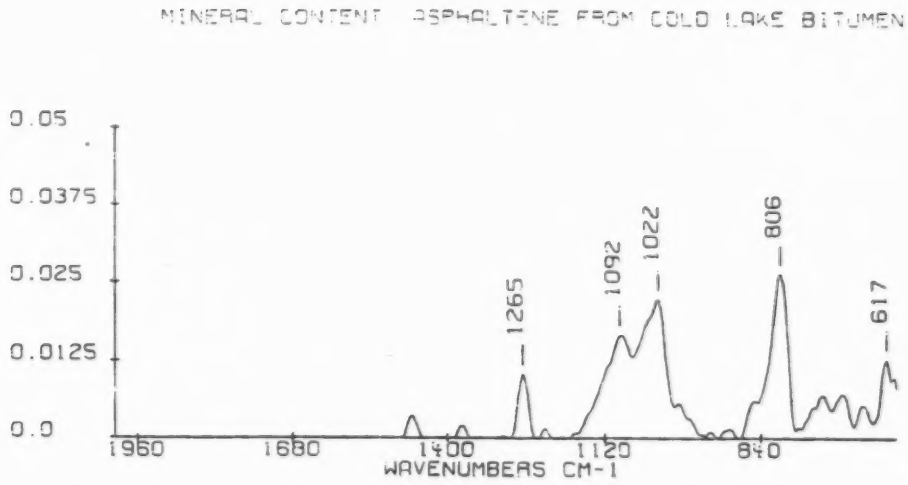


FIGURE 63

MINERAL CONTENT IN ASPHALTENE FROM COLD LAKE BITUMEN

5b



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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FIGURE 64

1 ASPHALTENE FROM HYDROGENATED ATHABASCA BITUMEN

2 DEMINERALIZATION PRODUCT FROM 1

6

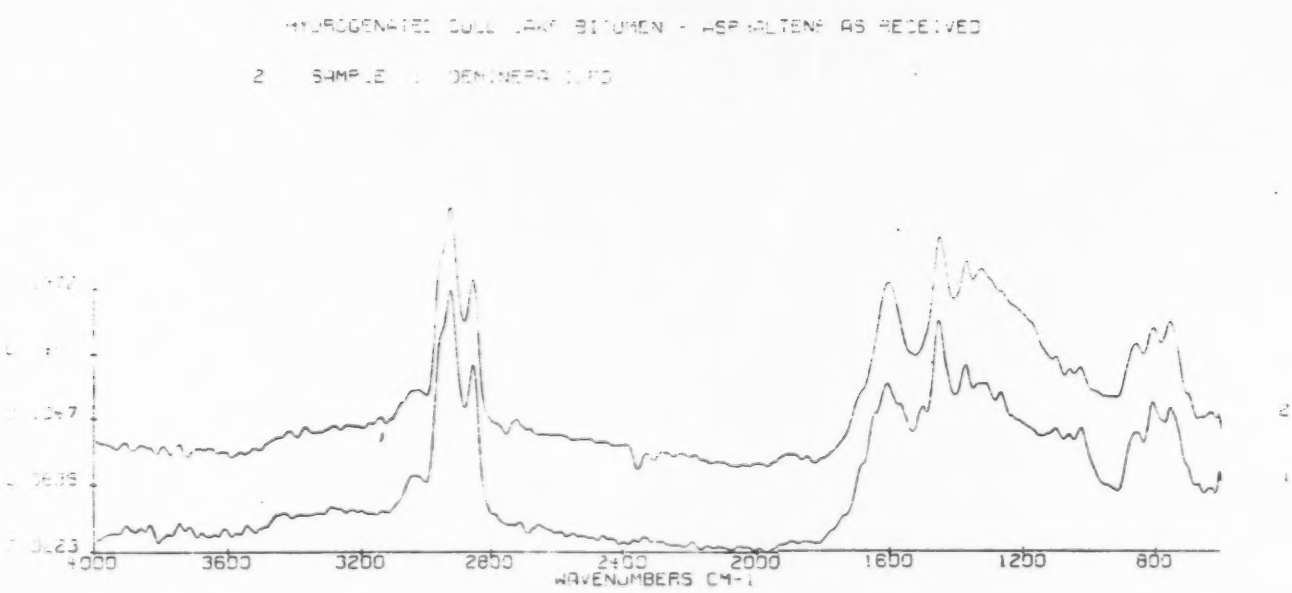

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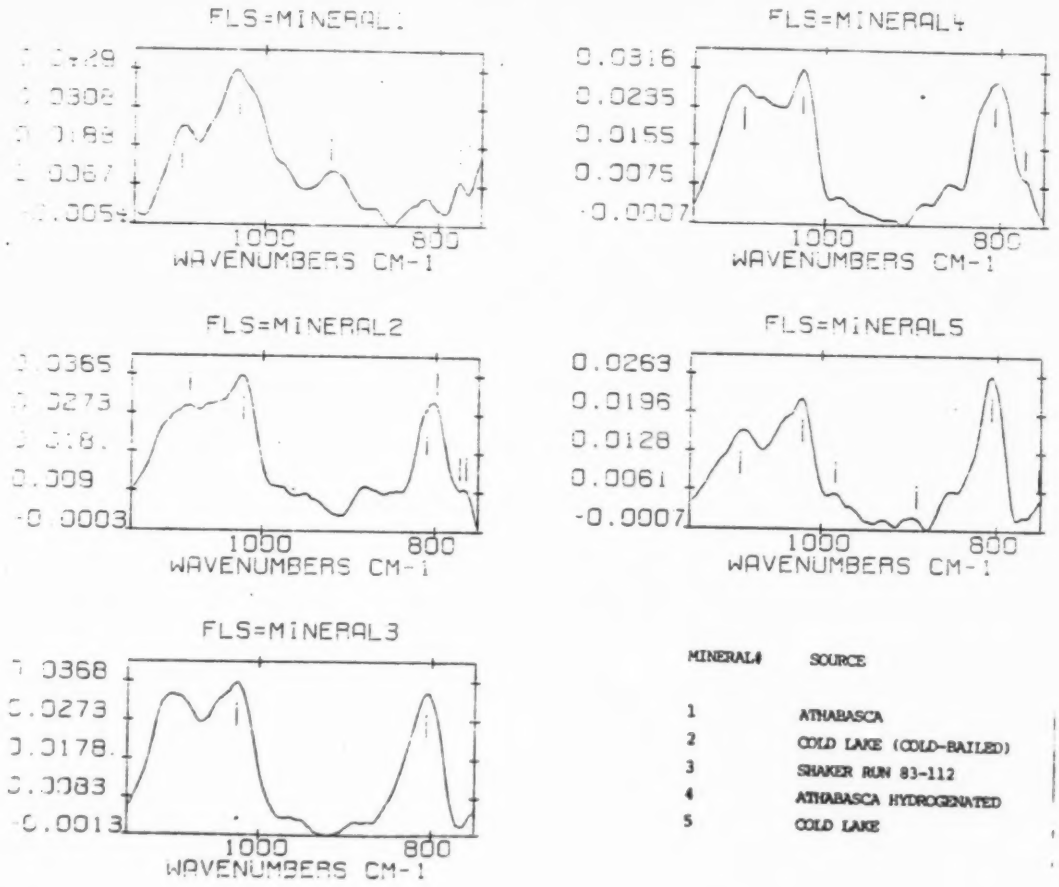
FIGURE 65

DIFFERENT MINERAL TYPES IN ASPHALTENES

1 ATHABASCA 2 COLD LAKE, COLD-BAILED 3 SHAKER RUN 83-112

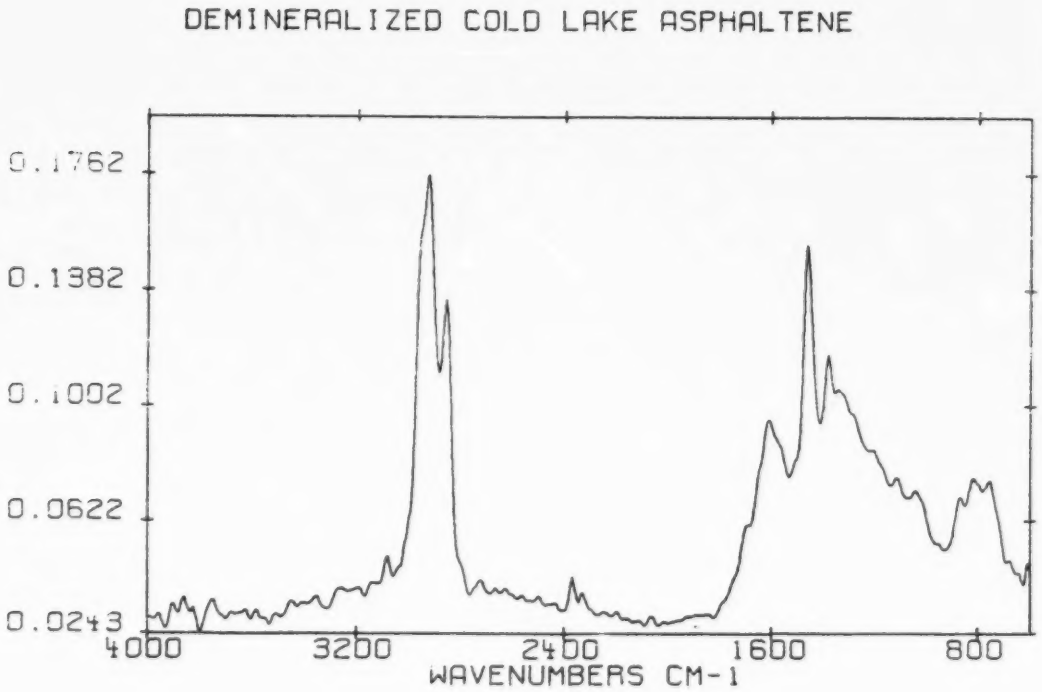
4 ATHABASCA HYDROGENATED 5 COLD LAKE



MINERAL#	SOURCE
1	ATHABASCA
2	COLD LAKE (COLD-BAILED)
3	SHAKER RUN 83-112
4	ATHABASCA HYDROGENATED
5	COLD LAKE

FIGURE 66

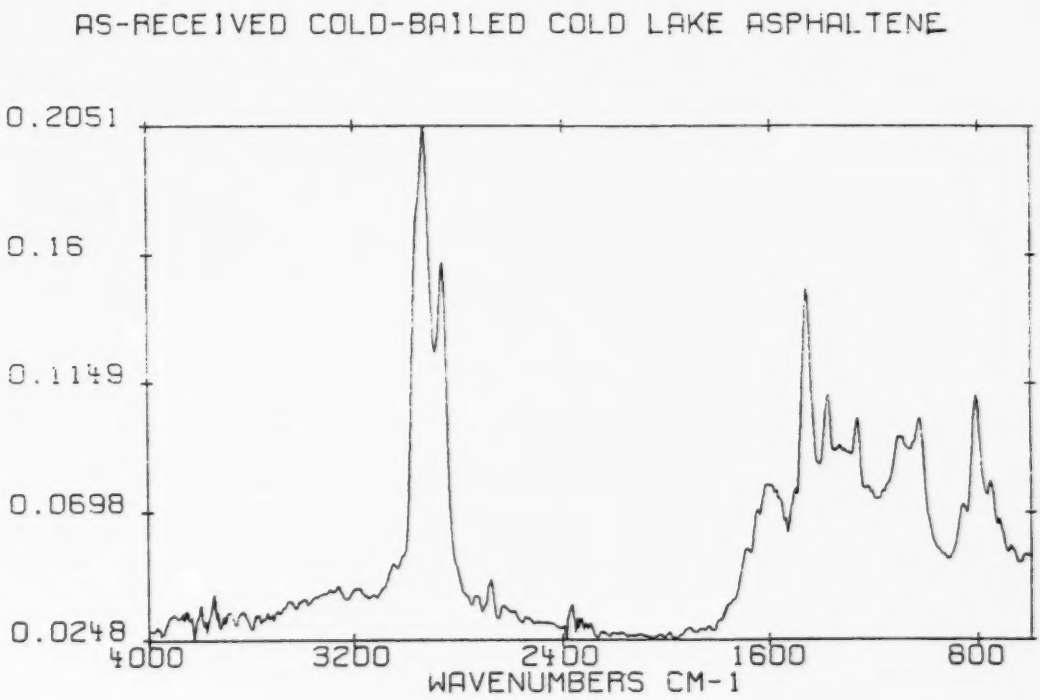
DEMINERALIZED COLD LAKE ASPHALTENE



79

FIGURE 67

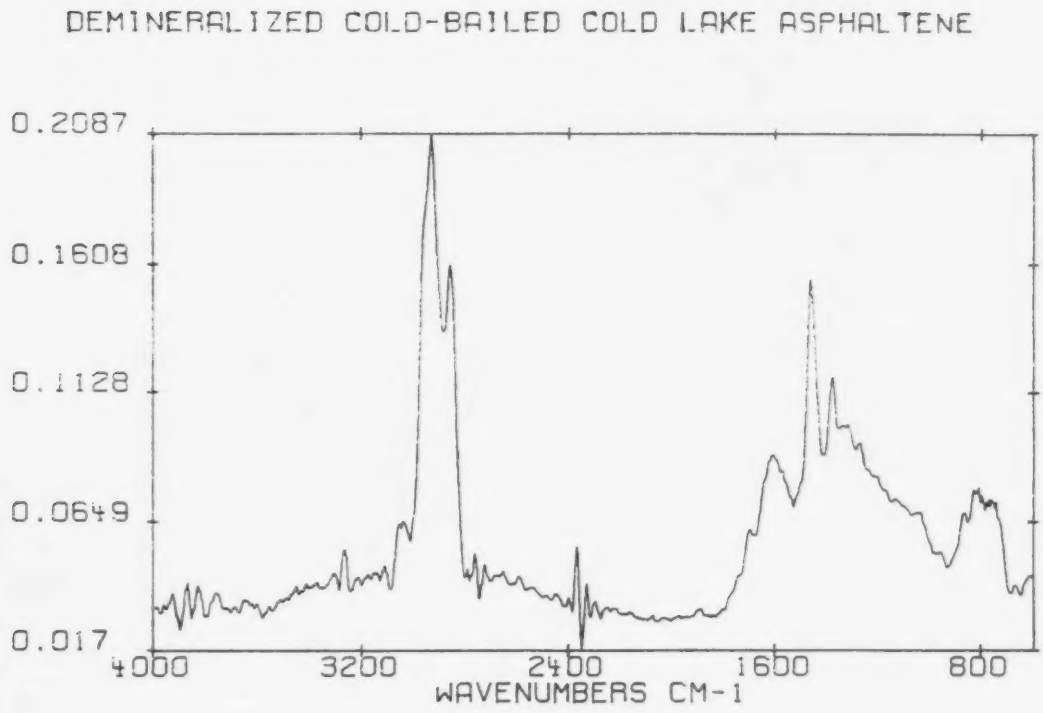
AS-RECEIVED COLD-BAILED COLD LAKE ASPHALTENE



80

FIGURE 68

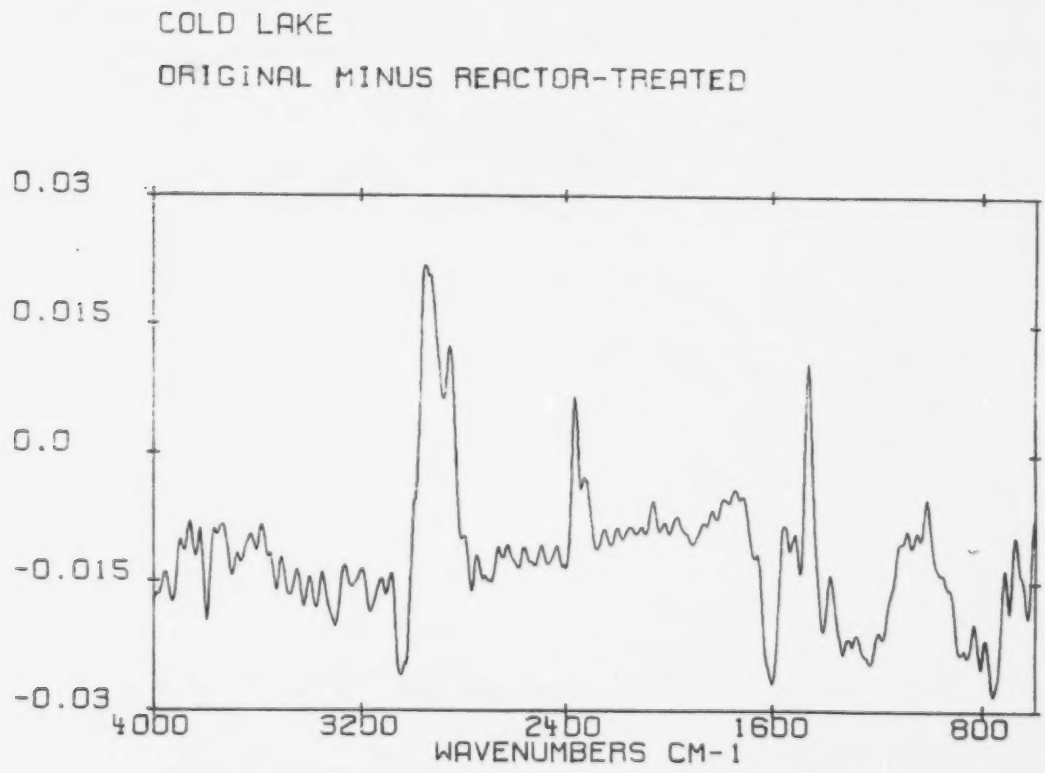
DEMINERALIZED COLD-BAILED COLD LAKE ASPHALTENE



81

FIGURE 69

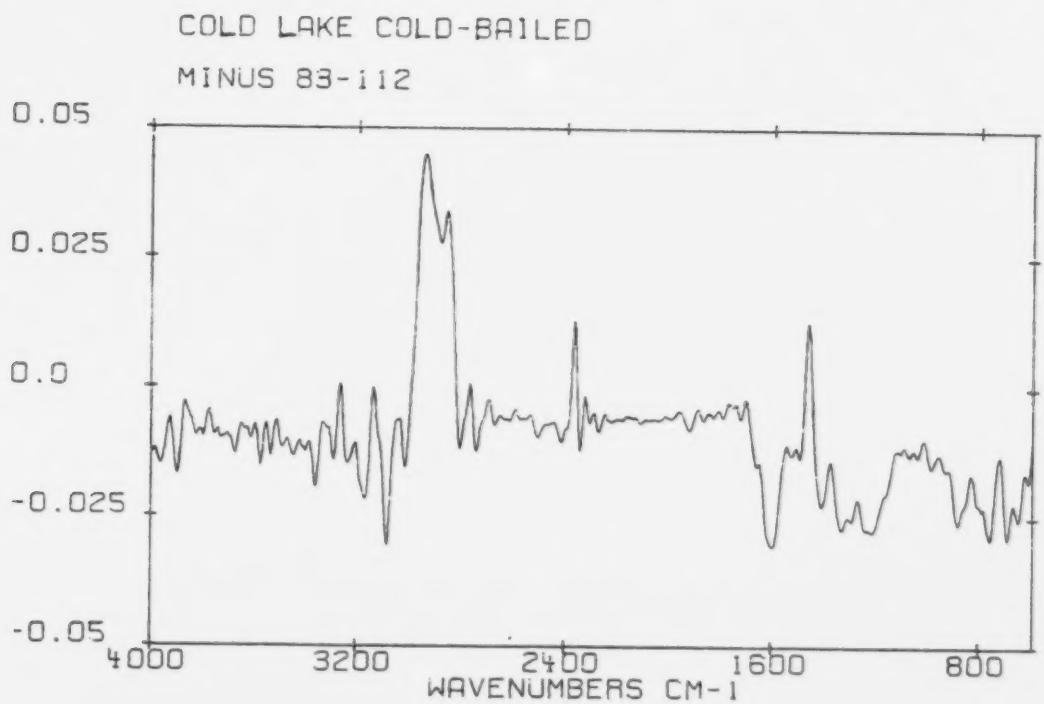
ASPHALTENES FROM COLD LAKE BITUMENS -
ORIGINAL minus REACTOR-TREATED



82

FIGURE 70

ASPHALTENES - COLD LAKE COLD-BAILED MINUS 83-112

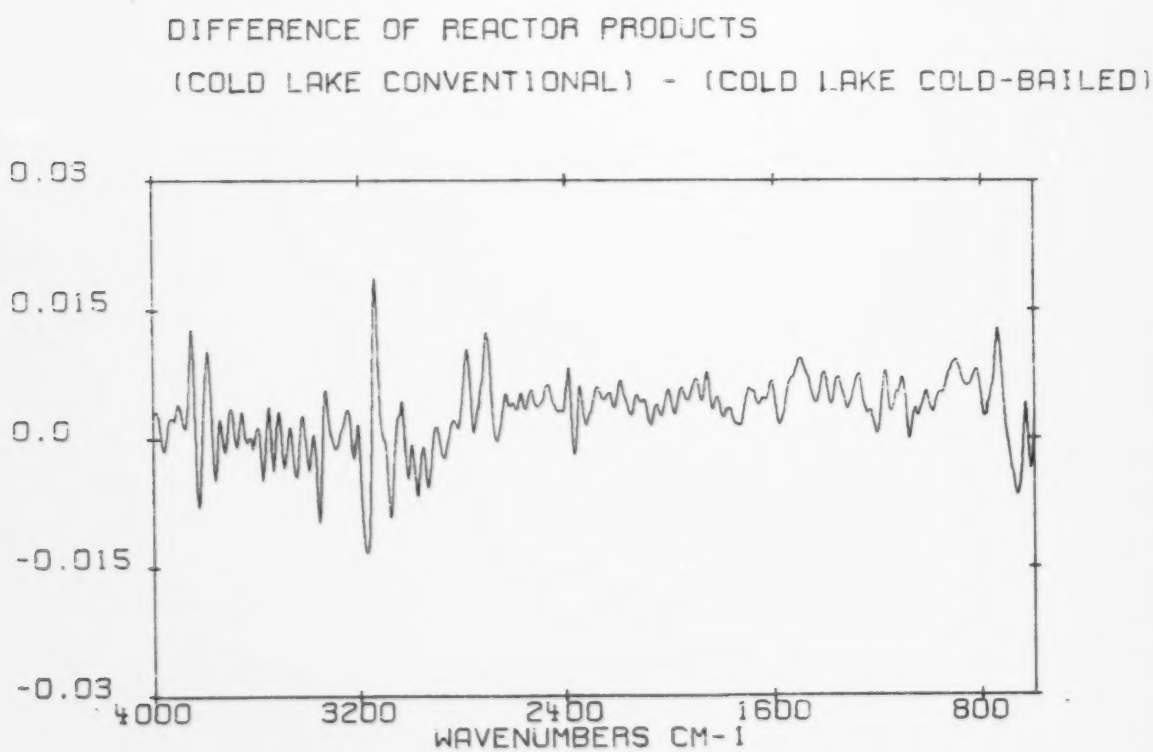


83

FIGURE 71

DIFFERENCE OF REACTOR PRODUCTS

(COLD LAKE CONVENTIONAL) minus (COLD LAKE COLD-BAILED)

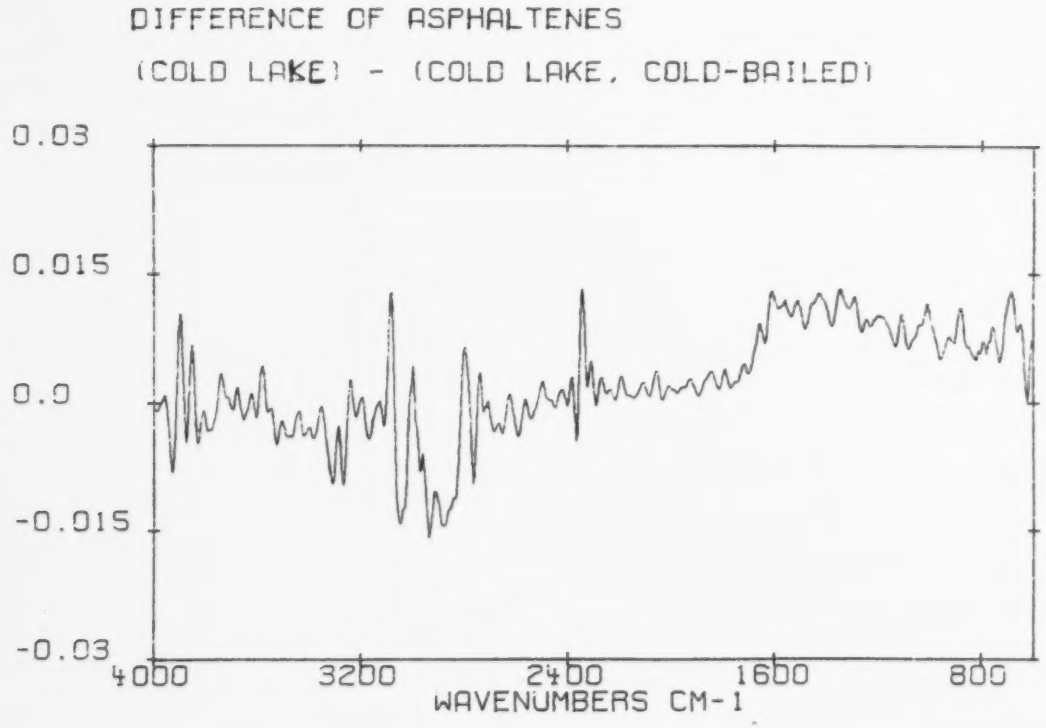


84

FIGURE 72

DIFFERENCE OF ASPHALTENES

(COLD LAKE) minus (COLD LAKE COLD-BAILED)



BITUMINOUS COALS OXIDIZED AT 50°C UNDER 1400 KPa AIR PRESSURE

The samples provided for spectroscopic examination were Cape Breton (Devco) bituminous coal samples P-303 and P-304.
We were informed that the P-303 sample was richer in vitrinite and had a lower mineral content than P-304.

The attached spectroscopic information includes full spectral displays of the various samples, oxidized for periods from 0 to 168 h, and difference spectra between 2000 and 1400 cm^{-1}

These are reproduced as Figures 73 through 82.
Samples are identified in the format 303/h where h is the oxidation period in hours. A commentary is reproduced as Table 8.

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

TABLE 8

COMMENTARY ON OXIDIZED SAMPLES

1985 April 04

Dr. J. A. MacPhee
Research Scientist
CANMET/Energy Research Laboratories
Energy, Mines, and Resources Canada
555 Booth Street
Ottawa, Ontario K1A 0G1

Dear Tony:

I enclose the PAIFT spectra of the samples of variously oxidized coals # 303 & 304, and the difference spectra.
The difference spectra are the more informative, but the changes in the "304" samples are at the limits of detection for the 48 and 72 hour oxidations. Also, the "303" samples seem to have undergone approximately the same extent of superficial oxidation after 48, 72, & 96 hours; further carbonyl intensity has developed after 168 hours.
As I mentioned on the telephone, the "303" fraction appears to oxidize appreciably faster than the "304". It will be interesting to see if this can be accounted for in terms of differing pyritic content.

I am visiting Edmonton CRL next week and hope to have the final report on "Phase II" ready shortly thereafter, together with some suggestions for a further "Statement of Work".

With all good wishes,

Yours sincerely,

Brian M. Lynch

Brian M. Lynch
Professor & Chairman, Department of Chemistry

PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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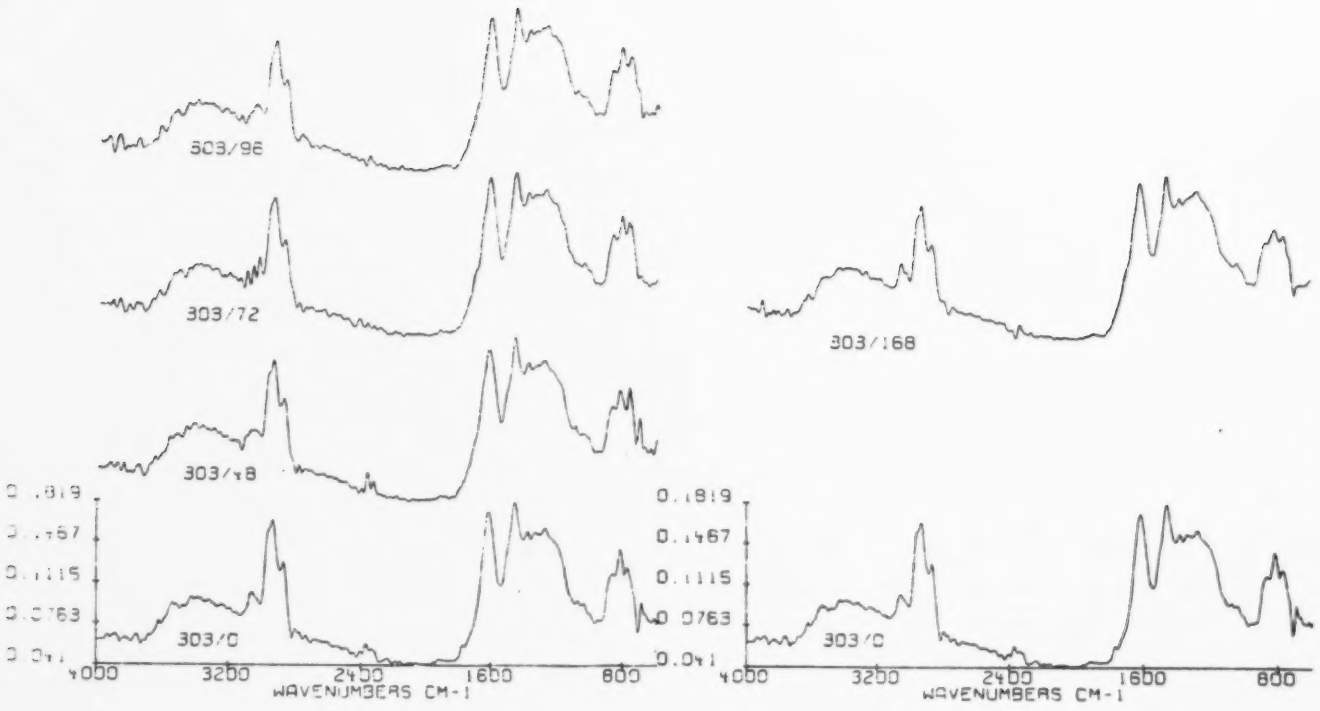
FIGURE 73

PAIFT SPECTRA OF P-303 SAMPLES OXIDIZED FOR VARYING PERIODS

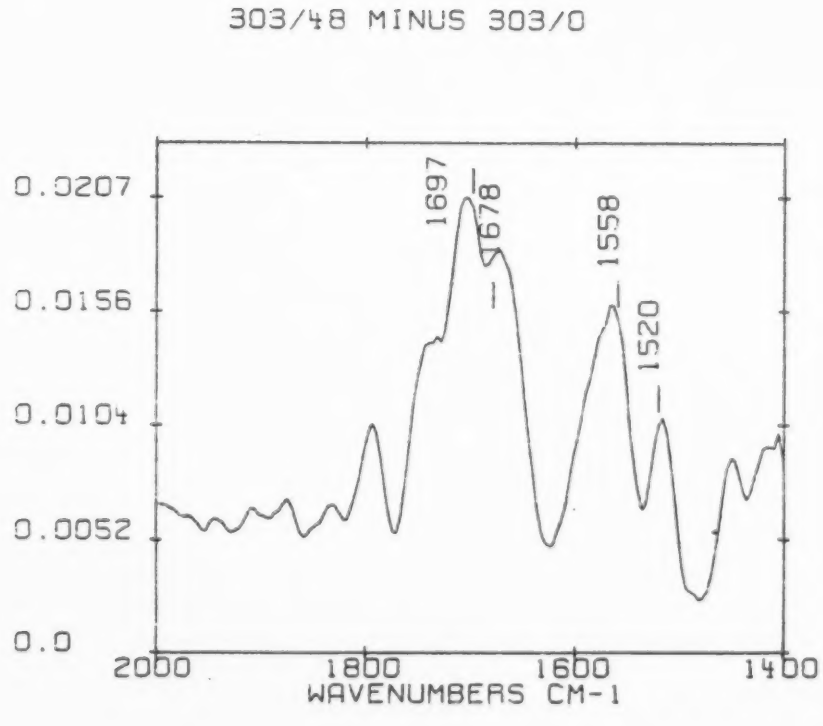


88

FIGURE 74

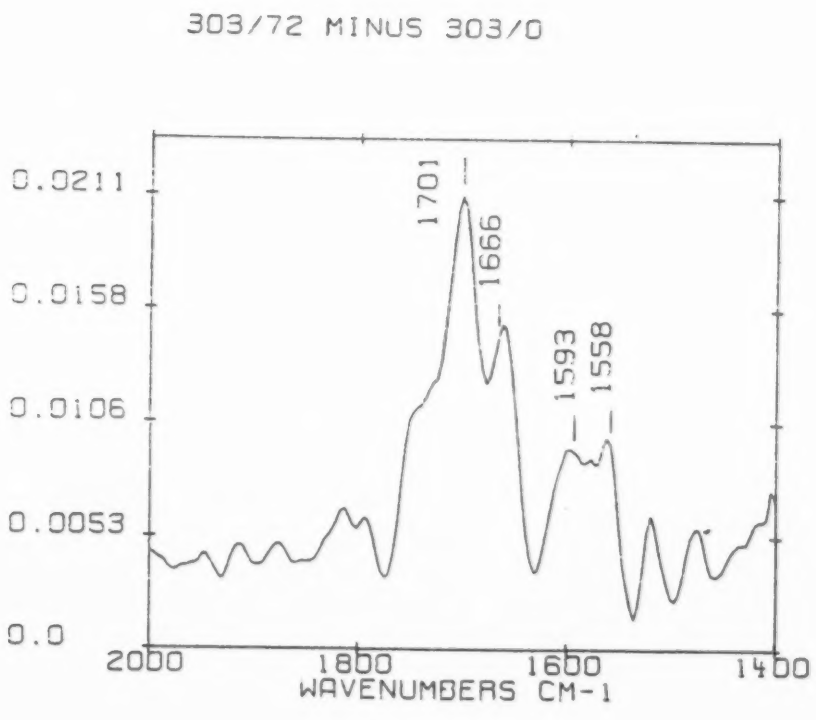
DIFFERENCE SPECTRA

303/48 minus 303/0



89

FIGURE 75
DIFFERENCE SPECTRA
303/72 minus 303/0

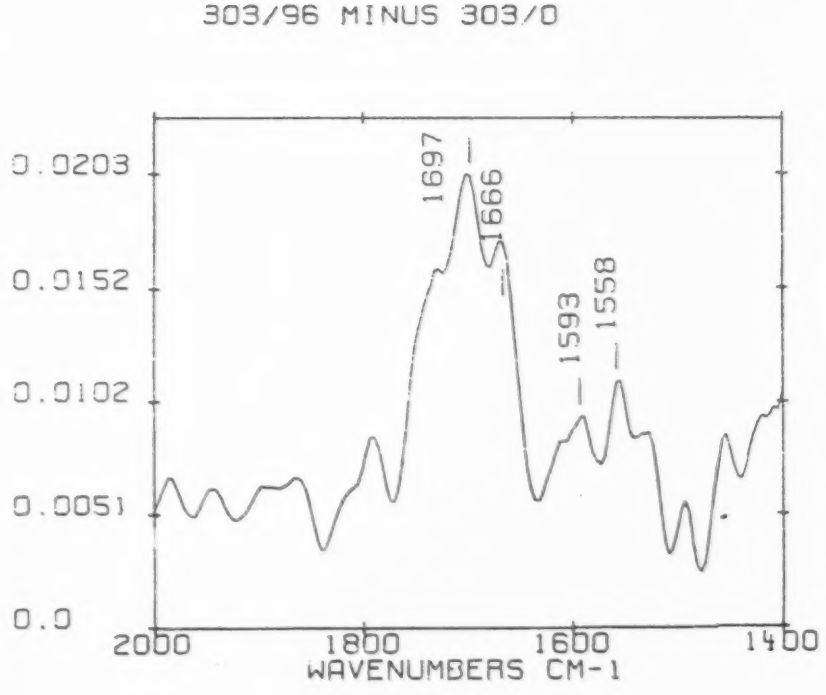


90

FIGURE 76

DIFFERENCE SPECTRA

303/96 minus 303/0

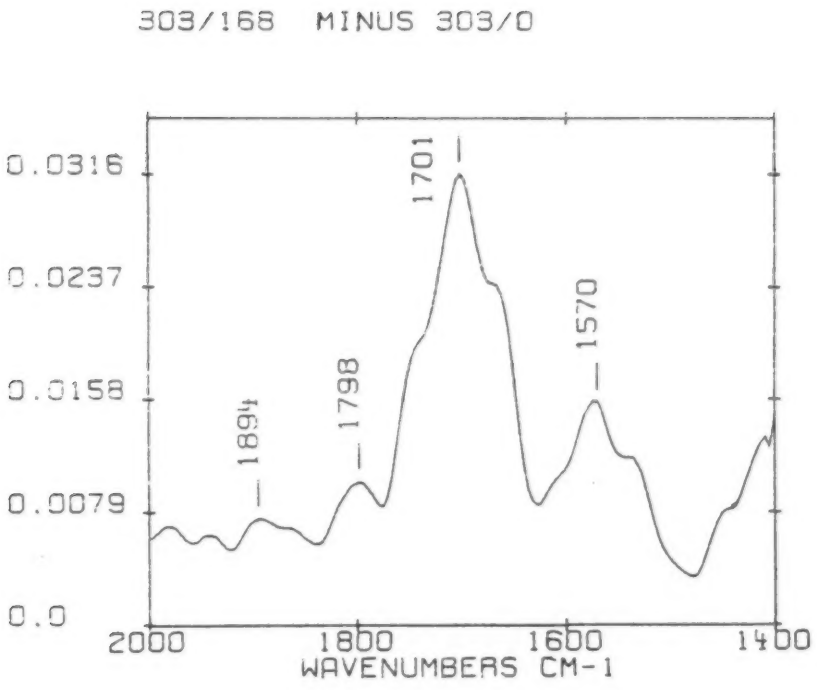


91

FIGURE 77

DIFFERENCE SPECTRA

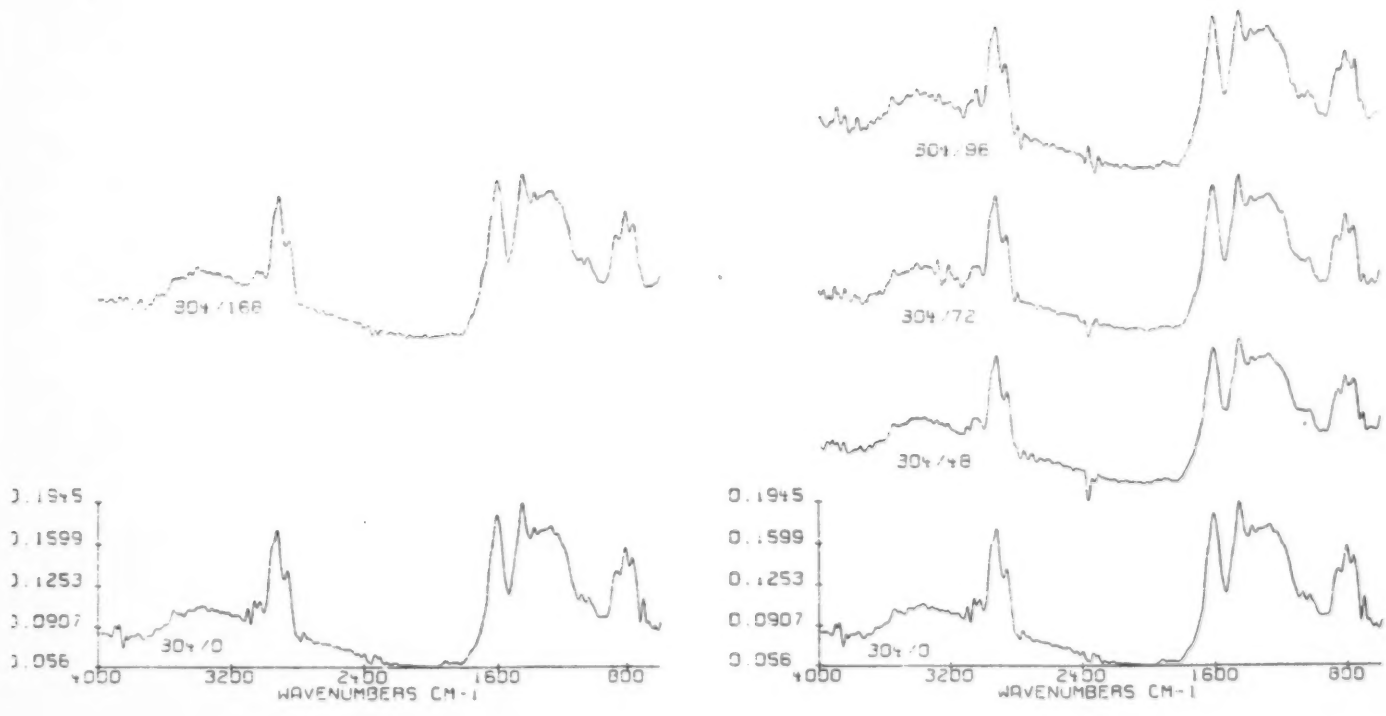
303/168 minus 303/0



92

FIGURE 78

PAIFT SPECTRA OF P-304 SAMPLES OXIDIZED FOR VARYING PERIODS



93

FIGURE 79

DIFFERENCE SPECTRA

304/48 minus 304/0

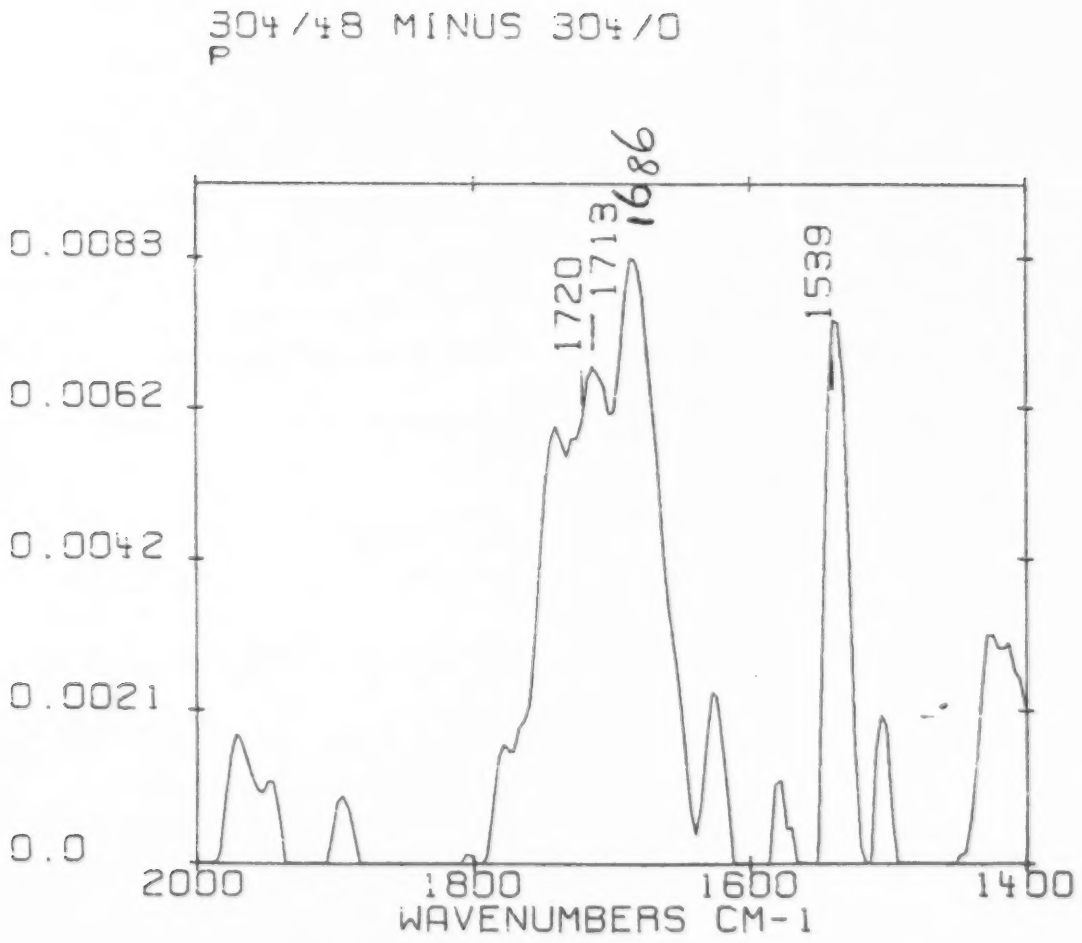


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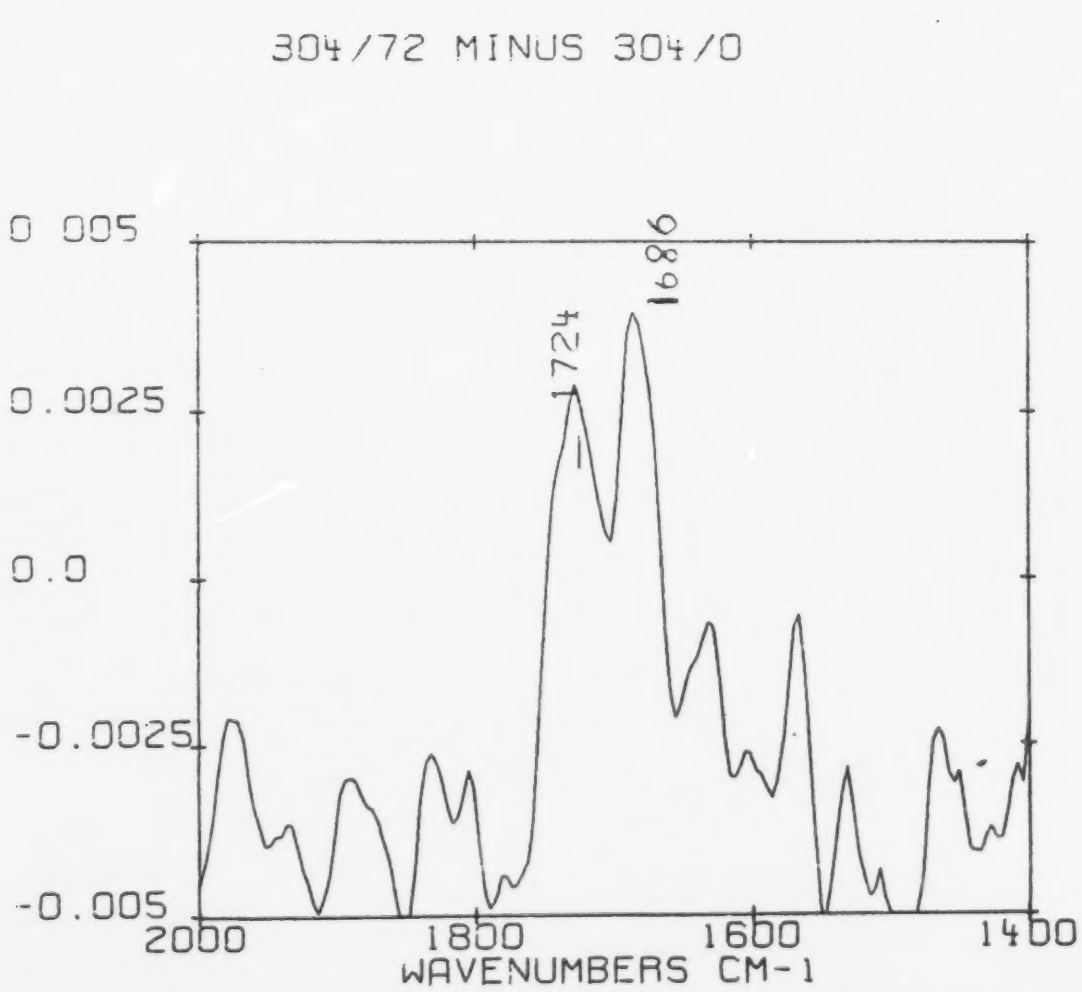
FIGURE 80

DIFFERENCE SPECTRA

304/72 minus 304/0

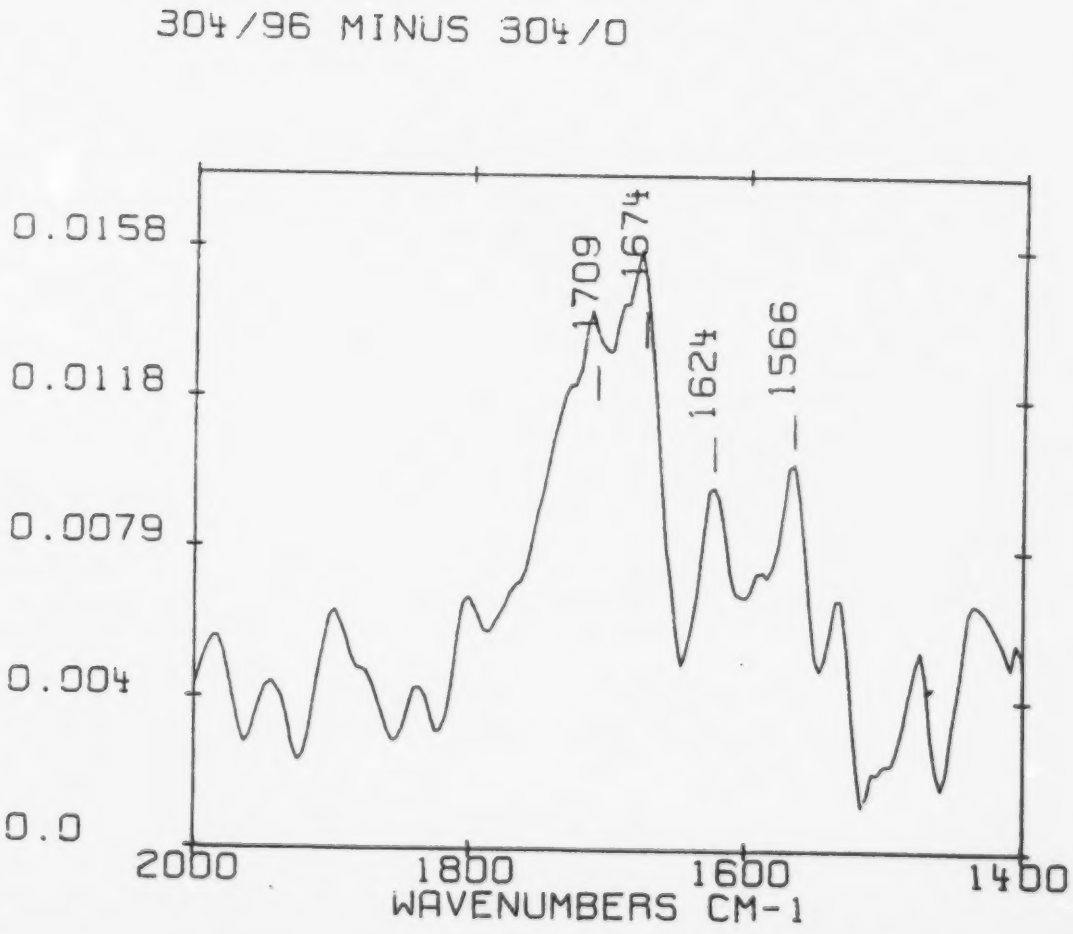


95

FIGURE 81

DIFFERENCE SPECTRA

304/96 minus 304/0



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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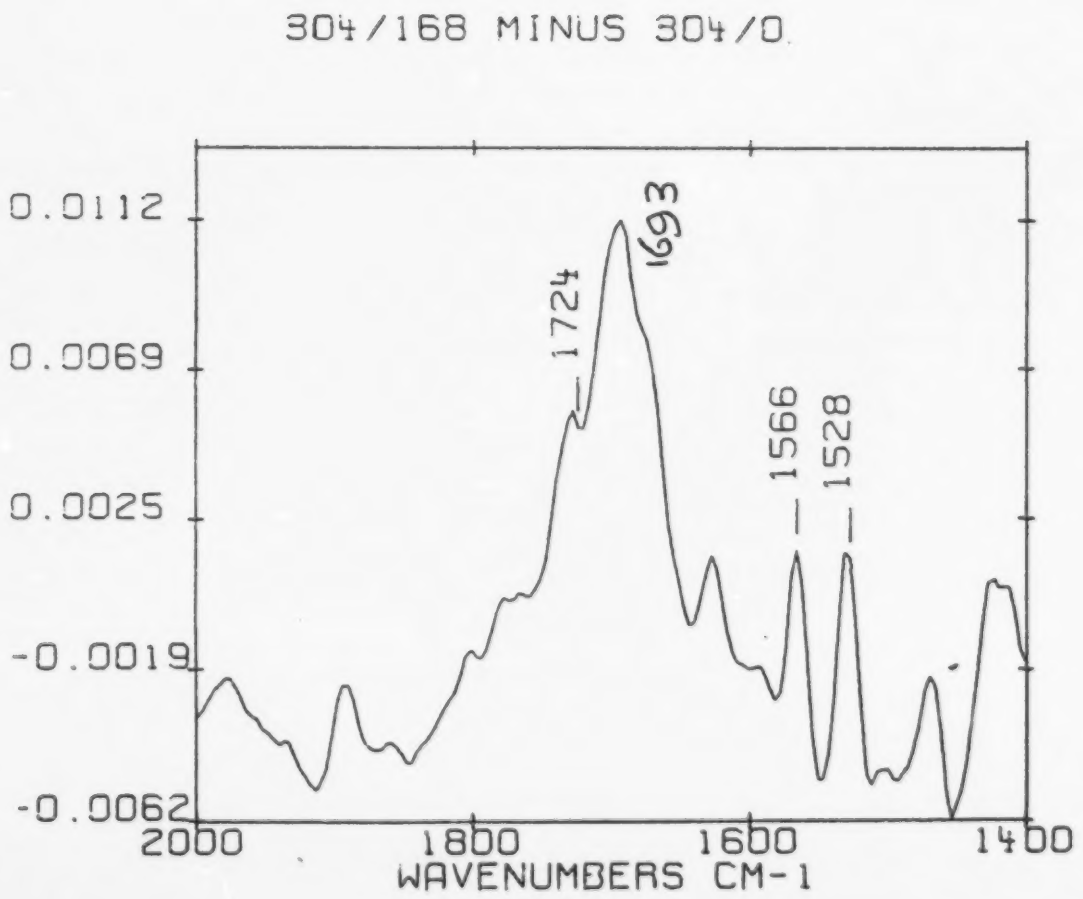
FIGURE 82

DIFFERENCE SPECTRA

304/168 minus 304/0



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FOR STUDY OF COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE II

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GENERATION OF CARBONYL FUNCTIONALITY IN BITUMINOUS COALS BY TREATMENT WITH BASES AND BY VACUUM THERMOLYSIS

In the course of derivatization of bituminous coal samples by a modification of the phase-transfer methylation technique used by Liotta and his co-workers (4), we observed that the carbonyl-region infrared absorptions of many coals were enhanced as compared with the parent samples, even for supposedly fresh, unoxidized coals (see Figure 83).

The added carbonyl absorption is introduced at the stage of coal anion formation, where the coal is treated under a nitrogen atmosphere with a solution of tetrabutylammonium hydroxide in aqueous tetrahydrofuran.

The implication is that new carbonyl groups are introduced by a process accompanying coal anion generation.

I believe that the accompanying reaction is one of base-promoted elimination involving a peroxide or hydroperoxide species present in significant concentration at the coal surface, i.e.-

$$OH^- + R_2CH.O.O.H \longrightarrow R_2C{:}O + H_2O + OH^-$$
$$\text{or } OH^- + R_2CH.O.O.R \longrightarrow R_2C{:}O + H_2O + O.R^-$$

Such reactions are well documented in model systems (5-7).

The extent of generation of carbonyl species by base-treatment is dependent upon the history of the coal, and increases with time of laboratory storage. This is to be expected; the surprising aspect is that such a relatively straightforward possibility has not been considered previously.

I ascribe previous failures to observe similar behavior to the deficiencies of classical KBr-pellet transmission infrared sampling, where the fine grinding disperses any surface functionality uniformly through the coal matrix so that the proportion of detectable carbonyl absorption is lowered below the level of detection.

Figures 84 through 86 illustrate through difference spectra a progressive increase in the base-generated carbonyl content in three samples of Devco bituminous coal.

The first (P-302) was stored under water and ground on-site, the second (P-303) was supplied to us by ERL in mid-1984, and the third (P-304) had been stored in a laboratory vial since 1983. This is good, consistent evidence that the proportion of surface peroxide increases with time of laboratory exposure.

The postulated surface peroxides would be expected to be decomposable thermally to generate carbonyl (and also ether) species (7), and vacuum thermolysis of several coals reveals such development.

Figures 87 through 89 illustrate the vacuum thermolysis at 200°C of the same three samples which had been subjected to base-treatment (see above).

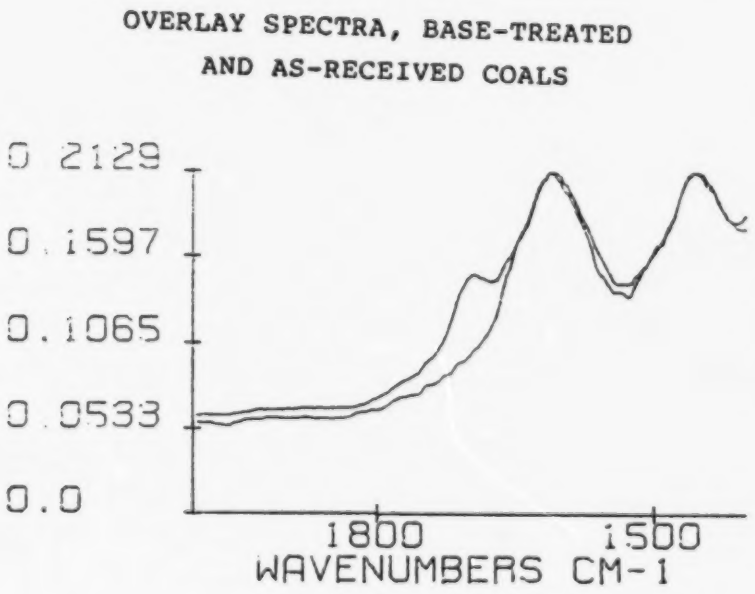
The consequences of this new finding about the nature of surface oxygen in bituminous coals are being explored further through an EM & R Research Agreement (8).

Two recently discovered aspects of particular interest are that selective introduction of carbonyl functions can be driven at room temperature by bubbling air through a suspension of coal in a solution of tetrabutylammonium hydroxide in aqueous tetrahydrofuran, and that the carbonyl functions are cleanly and quantitatively reducible by tetrabutylammonium borohydride.

It is hoped that these findings may be explored further in an extension of this study.

FIGURE 83

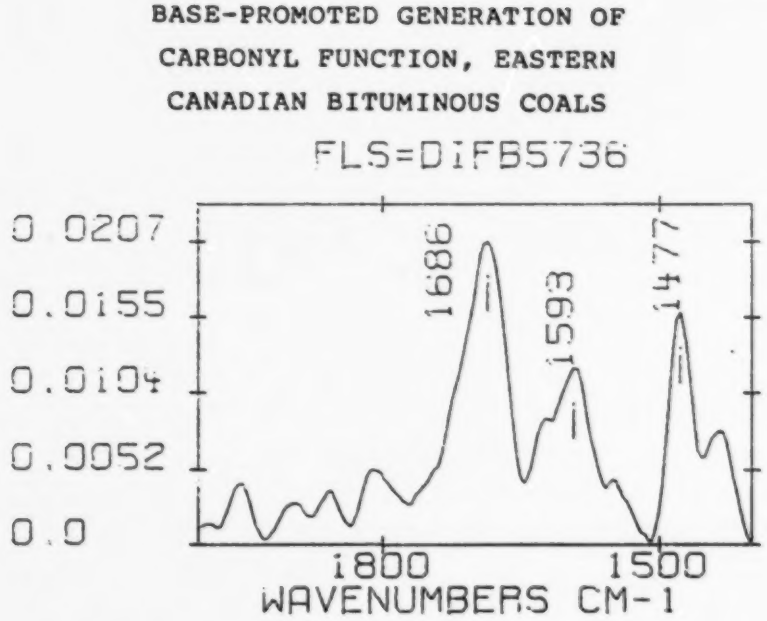
OVERLAY SPECTRUM, BASE-TREATED AND AS-RECEIVED COAL P-303



100

FIGURE 84

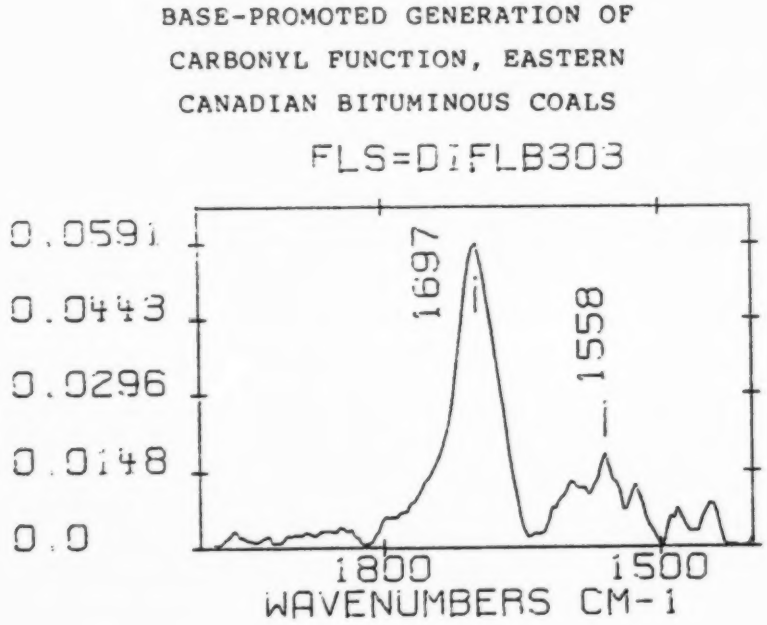
DIFFERENCE SPECTRUM REVEALING BASE-PROMOTED GENERATION OF CARBONYL FUNCTION, BITUMINOUS COAL P-302 STORED UNDER WATER



101

FIGURE 85

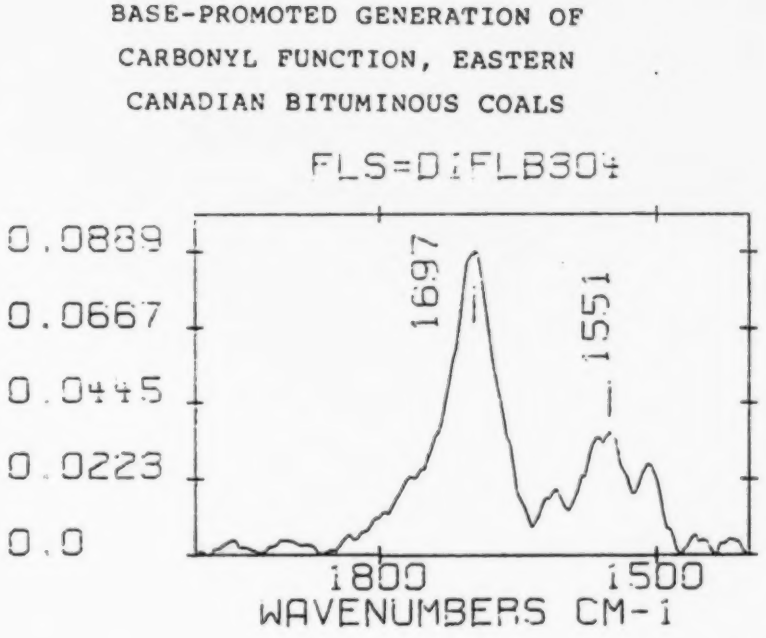
DIFFERENCE SPECTRUM REVEALING BASE-PROMOTED GENERATION OF CARBONYL FUNCTION, BITUMINOUS COAL P-303



102

FIGURE 86

DIFFERENCE SPECTRUM REVEALING BASE-PROMOTED GENERATION OF CARBONYL FUNCTION, BITUMINOUS COAL P-304



PHOTOACOUSTIC FTIR SPECTROSCOPY AS AN ANALYTICAL TOOL
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FIGURE 87

DIFFERENCE SPECTRUM REVEALING VACUUM-THERMOLYTIC GENERATION OF CARBONYL FUNCTION, BITUMINOUS COAL P-302

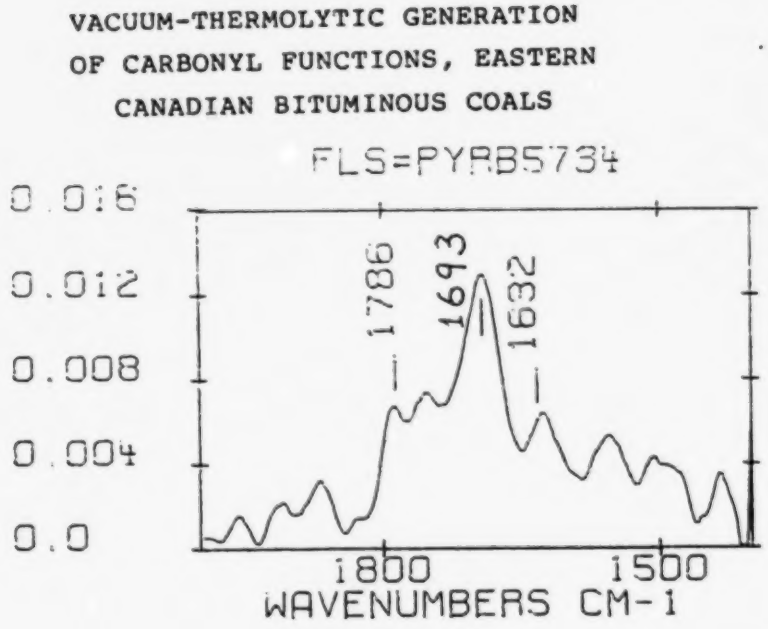

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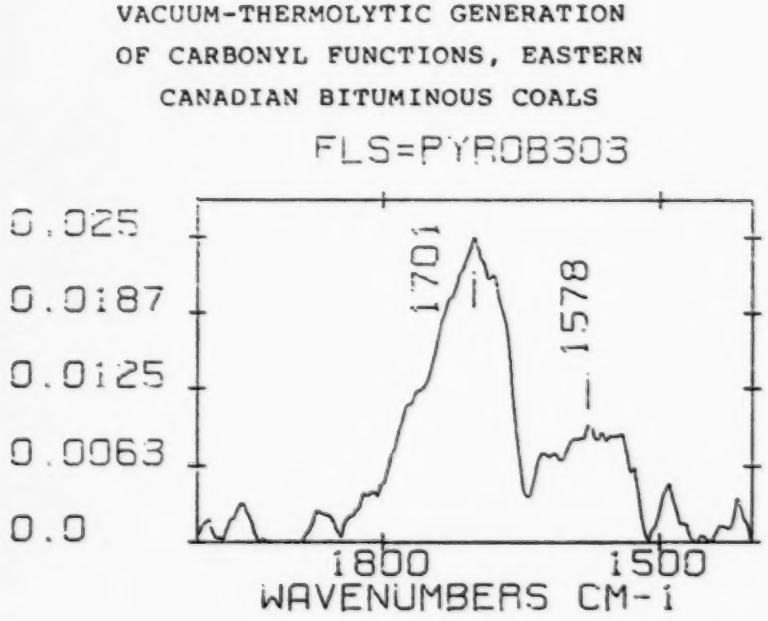
FIGURE 88

DIFFERENCE SPECTRUM REVEALING VACUUM-THERMOLYTIC GENERATION OF CARBONYL FUNCTION, BITUMINOUS COAL P-303



ACKNOWLEDGEMENTS

I thank Mrs. Lai-Im Lancaster of this Department for her many contributions to the experimental and practical aspects of the work reported here.

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